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CONTENTS

VOLUME 1

Biochemistry of Biophoton Emission
-Reaction Pathways and Emitters-

Haruo Watanabe
Biochemical Information Group

Biophoton phenomena are understood to be ultraweak chemiluminescents from living organisms, based on biological oxidation. The occurrence of biophoton is observed on the various biological substances, such as amino acids and lipids. In addition, biophoton emission is widely distributed in the biological world, from microorganisms to human bodies. According to modern innovation and recent development of ultrahigh sensitive photon counting and data analyzing techniques, it is considered that biophoton emission occurs generally in all organisms. The biophoton emission is generated from chemically excited states of fluorescent compounds in the organisms. The oxidation of biological substances by oxygen species leads to acquisition of highly energized states. Especially on the mechanism of biophoton emission, the role of active oxygen species generated in bodies are important as biological oxidants for biophoton emission.

In this report, we described and discussed the process of formation of excited molecules from luminescent compounds and oxygen species in biophoton reactions. Together with the experimental results on reaction mechanism of biophoton emission, an evolutionary relationship between biophoton emission and rather strong bioluminescence is also discussed from a viewpoint of analogous molecular structures and similar reaction systems.

Shinkai Chemirecognics Project
-Molecular Design of New Chemirecognics From 'Calixarenes'-

Seiji Shinkai
Project Director

Living organisms contain chemical reaction mechanisms, such as enzyme reactions, which are highly efficient and highly selective. They also contain mechanisms such as antigen-antibody reactions, which accurately distinguish targets. The basis for these mechanisms is thought to be recognition through complex host-guest interactions. Efforts to artificially construct systems which show a high degree of recognition and establish methods of molecular design (not limited to particular hosts) will not stop at simply reproducing what is in nature: They may very well generate entirely new recognition mechanisms and targets.

In order to artificially realize superior recognition, it is necessary to have complex interactions between hosts and guests on the basis of multipoint interactions. Calixarene[1] is a recently synthesized ring compound which can do this by inclusion of the guest. Calixarene and its analogues give rise to a lock-and-key positioning of the molecules and atoms of the guest and host through the intricate positioning of hydrogen bonds, coordination bonds, hydrophobic interactions, electrostatic interactions, and CH-π interactions.[2] This produces excellent selectivity. Moreover, changes in the shape of the hole can produce recognition of the three-dimensional structure of the guest.

This project will explore the relationship between the molecular structure of the host and its recognition properties. Through modifications, the project will also seek to make inclusion recognition systems with special selectivity towards metal ions and organic molecules. These modifications to calixarene will involve introducing heavy metal coordination groups and functional groups. In this way, the project will study the relationship between the coordination groups and functional groups and any multipoint recognition interactions which arise. In addition, the project will seek to make artificial enzymes to introducing catalytic groups, and will make assemblies of calixarene to search for new functions which cannot be obtained singly.

This research, by establishing methodology for designing recognition, may lead to superior molecular sensors and artificial enzymes with high selectivity, environmental resistance, and utility—all in an artificial system.

Footnotes

1. Calixarene: A ring compound which can be synthesized to have three to eight benzene rings in a larger ring.
2. CH-π interaction: Interaction between the positively charged alkyl groups of an aliphatic carbon compound and the negatively charged electrons of a benzene ring.

Mizutani Plant Ecochemicals Project
-Why Are Wild Plant Species Strong?-

Junya Mizutani
Project Director

Among organisms higher plants cannot move their location, but they adapt themselves to the given environment and are equipped with defensive and offensive mechanisms to protect themselves and promote the growth of their species. This defense system has been acquired during the long process of evolution, and here chemical substances (plant ecochemicals) play an important role.

Green plants produce hundreds of thousands of compounds that are not involved in primary metabolism. The specific functions of these so-called secondary metabolites are largely unknown. Recently, the essential role that secondary compounds such as phenolics, terpenoids, and alkaloids play in complex interactions among living organisms in natural environment is gradually being unraveled. Rapid and radical advances in analysis technology have made it possible to isolate even minute amounts of ecochemicals and to perform sophisticated structural analyses.

We have already isolated many secondary metabolites from a variety of plant species, especially wild plant species, and tried to make their roles clear. In this project we aim at isolating and identifying plant ecochemicals; studying their formations in plants, roles in interactions among living organisms, and fates in environment; and further seeking the possibilities of their applications in agriculture and food, and human health. We are interested in defense substances which are produced by inducing physical, chemical, or biological stress. One part of this project is attempting to further develop the capabilities of analytical techniques as well as various bioassay processes.

The main subjects of the research groups are as follows:

1. Formation Mechanisms Research Group

The biosynthesis and metabolism of ecochemicals and their various adjustment mechanisms are being studied. This is being done while carefully analyzing the defensive mechanism of wild plant species. Deliberate simulation is also employed in order to explore the diverse defensive strategies of plants.

2. Allelochemicals Research Group

The evolution and role of ecochemicals in the interactions of wild plants with other plants or microorganisms are being studied as well as their

transformation into new physiologically active substances through the action of microorganisms.

3. Plant-Animal Interactions Research Group

Plant ecochemicals such as natural insecticides, repellents, and antifeedants are being studied by developing new bioassay systems which clarify the defensive mechanisms of plants against animals.

Role and Fate of Plant Defense Substances

Yasuo Kondo
Formation Mechanisms Research Group

The wild field plants are thought to have survived the fights against their enemies in nature and also to have taken advantage of the surrounding circumstances to reach an equilibrium state, thus enjoying the prosperity of their species in the environment. Consequently, they are expected to possess some strong or specific defense systems against the surrounding environment. In fact, many plants are known to have defense substances such as antimicrobial, insecticidal, allelopathy, and insect repellant compounds. The research objective of the Formation Mechanisms Research Group is to investigate the role and the fate of these compounds. Practically, we focus our research especially on antimicrobial substances and their induction and formation mechanisms.

To achieve this objective, we have surveyed more than 250 species of wild plants in Hokkaido for antimicrobial and other bioactivities and found that more than 90 species showed antimicrobial activities. This year, we isolated and characterized the active principles of several selected plants. This has led to the discovery of a number of compounds including several new substances. They are briefly as follows:

1. **From Caprifoliaceae**: Two phenolic antifungal compounds were found from *Viburnum furcatum* Blume.

2. **From Iridacea**: More than 20 flavonoids including eight new compounds were isolated from *Iris pseudacorus L.*

3. **From Compositae**: We found that two phenolic compounds (including one new), one elemophilane sesquiterpenoid, and four isomers of a sesquiterpene sulfoxide—new substances, which were the active components from *Petasites japonicus* Miq. We also found that *Erigeron annuus* produced a new pyrone derivative as the active component.

4. **From Rosaceae**: It was found that *Aruncus sylvester* Kostal produced four monoterpenoid antimicrobial compounds, as well as two nonactive but related substances, and they were all new compounds. Another Rosaceae plant, *Sorbaria sorbifolia* A. Br. Ver. *stellipilia* Maxim., *Malus baccata* var. *mandshurica* and *Spiraea salicifolia* L. were also investigated, from which three phenolic compounds and three new monoterpenoids were isolated and characterized.

We are still searching for new plants and compounds for interesting activities.

In addition to the above experiment, we also started the investigation on the induction mechanisms as we initially had planned. We have already found some active compounds and the plants that produce them. Many of the active components were produced by either wounding on the leaves or $CuCl_2$ aqueous solution, which means they were induced by these "stresses." We have been developing several new experimental model systems for the induction and the biosynthesis of those compounds. The experiments include, for example, the optimization of plant cell and tissue culturing conditions and the establishment of active components analyses. Another approach to this problem is the analyses of lipids and fatty acid hydroperoxides in the stressed plants. These hydroperoxides are known to be active components in damaged cells in animals, and they are also known to be produced in damaged plant cells. We try to estimate them by CL-HPLC and to find the exact relation between them and the induction of defense mechanisms.

Thus, we have found many active compounds from Hokkaido wild plants and are establishing the experimental systems with them to explore the plant defense mechanisms in nature. We would like to expand this project further and to apply the results to develop pollution-free pesticides and "self-defense" plants in the future.

Ecochemicals Associated With Plant-Plant and Plant-Microorganism Interactions

Hiroyuki Nishimura
Plant–Plant and Plant–Microorganism Group

All higher plants compete with each other for moisture, light, and soil nutrients in the ecosystem. In the course of this struggle, they have developed various means of defense against neighboring higher and lower plants. Ecochemicals associated with plant–plant and plant–microorganism interactions are called allelochemicals, i.e., growth inhibitors in the natural environment. Allelochemicals, secondary metabolites such as terpenoids and phenolics, etc., are exuded from plant roots or released from leaves. So far, potent allelochemicals have been isolated and identified from eucalyptus (*Eucalyptus* species), a mint plant (*Mentha spicata*), and lichens (*Usnea* species).

This report deals with plant growth inhibitors in sachaline giant knotweed (*Polygonum sachalinense*) and barnyard grass (*Echinochloa crusgalli*), and antimicrobial substances in chicory (*Cichorium intybus*) roots. First of all, allelopathy related to plant–plant interactions was evaluated using Stevens and Tang's root exudate recirculating systems. As bioassay, TLC–agar plate method was used to know RF value of the growth inhibitory test. The bioautography using *Cladosporium herbarum* was carried out to detect the antimicrobial substances on TLC.

Sachaline giant knotweed grows vigorously and promotes its territory to defend against other species in wild conditions. It is assumed that some growth inhibitors are exuded from the roots. The 80 percent acetone extract from the roots exhibited the germination and growth inhibitory activity. The extract was fractionated by SiO_2 column chromatography and two growth inhibitors were isolated by preparative HPLC using a reverse phase C_{18} column and MeOH–CH_3 CH–H_2O solvent system. From the interpretation of spectral data infrared radiation (IR), ultraviolet (UV), microscopy (MS), nuclear magnetic resonance (NMR)), the inhibitors were identified as emodin and physicion.

On the other hand, allelochemicals of barnyard grass, which competes with rice at the crop field, was examined. The extract from the whole plants exhibited growth inhibitory activities against several species. The *p*-Hydroxycinnamic acid and (*E*)–aconitic acid were isolated and identified as major growth inhibitors of barnyard grass against lettuce seedlings.

Antimicrobial substances in chicory roots as ecochemicals against micro-organism, e.g., fungi, were studied. White chicory shoots, which have been utilized as European salad and French dishes for a long time, are produced in a highly humid and dark room at ca. 15°C. Chicory roots keep from getting moldy even under these conditions.

The bioautography of hexane and ether extracts from chicory roots gave rise to the detection of several antimicrobial substances. As the results of repeating the liquid chromatography, e.g., HPLC, crystalline antimicrobial substances were isolated. These compounds were identified as sesquiterpene lactones such as guianolide and eudesmanolide by the interpretation of spectra data (^{1}H–^{1}H and ^{1}H–^{13}C COSY, etc.).

Furthermore, the mode of action concerning allelochemicals which have been identified was examined; SH–enzyme inhibition, respiration inhibition, α–amylase biosynthesis inhibition, etc. This subject is in progress.

Chemical and Biological Study of Allelochemicals Between Plants and Animals

Satoru Kawaii
Plant–Animal Interaction Research Group

Plant–animal interactions are currently being widely studied in order to provide better understanding of plant defense mechanisms. The Plant–Animal Interaction Research Group is actively involved in the development of new bioassay systems in order to estimate the action of the plant allelochemicals on other organisms, especially insects, acarians, and nematodes, and in the isolation and structure elucidation of allelochemicals.

(1) Screening of Hokkaido Plants for Antifeedant Activity Using an Improved Leaf-Disk Bioassay

Chemical elucidation of plant allelochemicals and study of their physiological mode of action are two fundamental steps for understanding the complex relationships between plants and other organisms. In this search for new bioactive compounds, we have undertaken a survey of Hokkaido plants where we have used an improved leaf–disk antifeedant bioassay against *Spodoptera litura* (tobacco cutworm). The principal improvement consists of a more accurate measurement of consumption rates using numeration of leaf–disk surfaces using a videocomputer interface. Among the 250 samples assayed, 33 were found to present a significant feeding–deterrent activity.

(2) Defensive Substances From Tropical Plants

Crude methanolic extracts of *Pavetta crassipes*, *Parkia clappertoniana*, and *Aristolochia albida* were examined for insect feeding deterrent activities against the armyworm larvae, *Spodoptera litura*, using a choice leaf–disk bioassay technique. TLC bioautography was also used for activity evaluation against the fungus *Cladosporium herbarum*. Only *A. albida* extract exhibited strong activity against *S. litura* and *C. herbarum*. Aristolochic acid, aristolic acid, and aristolactam were isolated and identified as feeding deterrent active compounds, and aristolone was identified as an antifungal principle.

(3) Two-Dimensional Analysis of Intracellular Ionized Calcium in the Nematode, *Caenorhabditis elegans*

Two–dimensional analyses of intracellular ionized calcium in a nematode were realized by using fluorescent dye (Fura 2–AM) and an image analyzer equipped with a SIT videocamera. The effects of several plant extracts on calcium concentration changes were examined by this method. Among them, a crude extract of damaged leaves of *Viburnum furcatum* "Okamenoki" showed an interesting pattern. Using a nematocidal activity bioassay as a monitor, chavicol and demethyleugenol were isolated and identified as active compounds

and they also exhibited the same pattern of calcium concentration change as the crude extract. Before adding chavicol, the pharynx and intestine wall were specifically stained and after addition the forepart of the intestine was brightly stained and the bright part gradually shifted to the rear intestine. From this result, chavicol and demethyleugenol had a significant effect on the intestine wall of the nematode.

This method allows the evaluation of the effect of physiologically active compounds on the nematode and this well-studied nematode coupled with Fura 2-AM would provide a method to study the role of calcium ions in living cells.

VOLUME 2

Sasaki Quantum Wave Project (1988~1993)
-Creation of Three-Dimensional Quantum Functional Structure and Electron Wave Control-

Hiroyuki Sasaki
Project Leader

1. Introduction

The quantum wave project has been underway for two years. Some of the principal facilities have started their operations, and research works have also begun to move along the set lines. Research results are also being obtained, though still preliminary. On this occasion, parts of the research activities will be presented, and we solicit your criticism and opinions.

2. Summary of Progress and Results of Research

2.1 Creation Technology of Three-Dimensional Quantum Functional Structures

For the realization of desired physical properties or functions through control of quantum waves, an active use of three-dimensional quantum structures is effective. For that purpose, establishment of a technology for forming quantum wires and quantum boxes (Figure 1) with cross sections smaller than 200 Å, without the use of lithography, is required. One formation method is the technique of forming electron confining layers on the edges of a quantum well (Figure 2). We investigated the formation of the edge quantum wire (E-QWI) by means of a new crystal growth method metal organic chloride-atomic layer epitaxy (MOC-ALE) and the molecular beam epitaxy (MBE) method and obtained several new results. These will be reported in more detail by Usui of the Quantum Hyperstructure Group and Kadoya of the Exploratory Devices and Physics Group.

The ALE method, excellent in film thickness controllability, is an attractive method, but it is not necessarily satisfactory as to the purity of the crystal obtained and the light-emission efficiency. It was confirmed that the newly developed MOC-ALE method is capable of forming GaAs and GaP of satisfactory quality while maintaining the advantages of the ALE method.

2.2 Formation and Electronic Properties of Quantum Hybrid Materials

Under the present project, the Quantum Hybrid Materials Group is in charge of exploring and elucidating the effects of quantum waves in the system of materials that includes materials other than the ordinary semiconductors. As a first step, we are examining whether an oligomer (a polymer) obtained by linking a predetermined number (n = 3~7) of thiophene molecules can be regarded as a kind of quantum box. This year we fabricated a field effect transistor (FET) for the purpose of investigating the movement of the holes

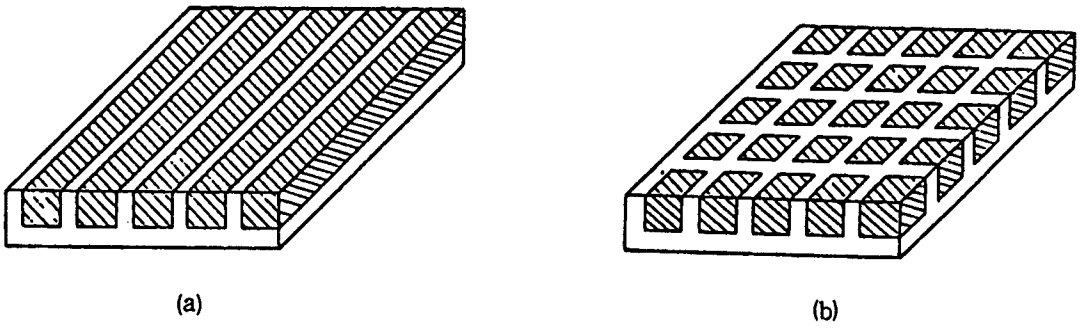

Figure 1. Conceptual View of (a) Quantum Wire and (b) Quantum Box

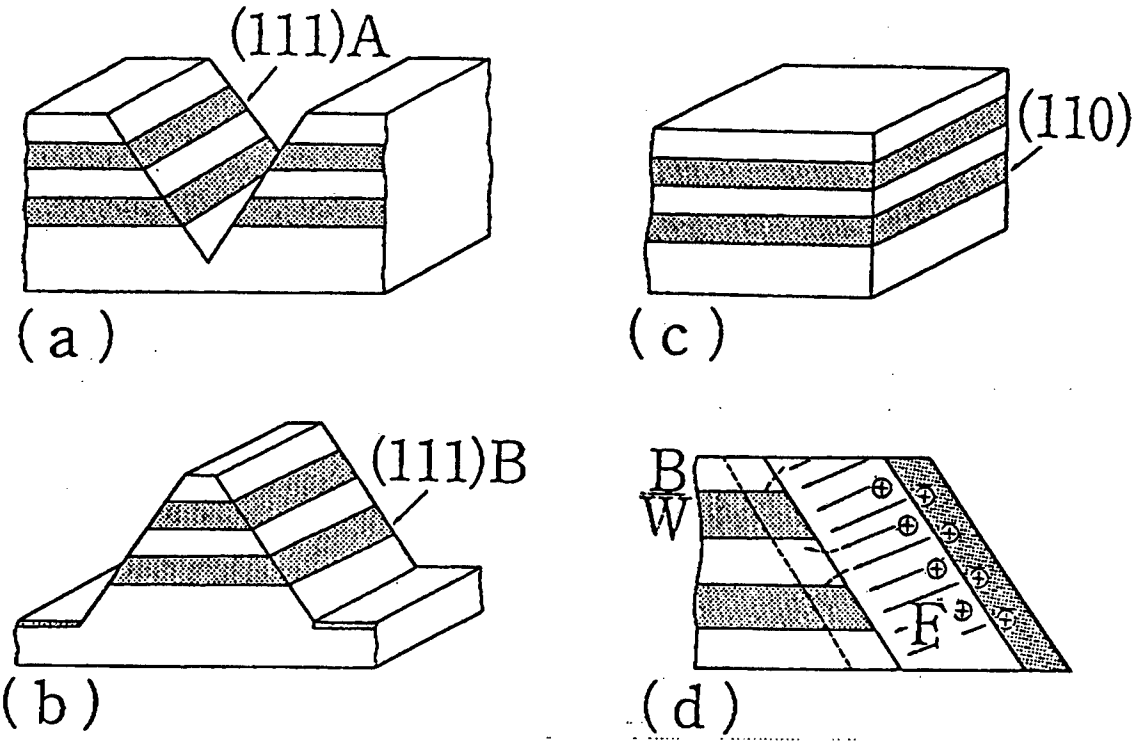

Figure 2. Conceptual Views of Edge Quantum Wires (E-QWIs)
(The edges of a quantum well are exposed by (a) using a V groove, (b) using a facet, or (c) using a cleavage plane, and (d) confining electrons within the surface parts.) (From Sasaki's works in 1976, 1980, and 1986.)

between the oligomers, and found that a satisfactory FET can be obtained. The details about this research, in particular the systematic change in the characteristic, etc., that accompanies the modification of both ends of the oligomer with alkyl group, will be reported by Hotta of the group.

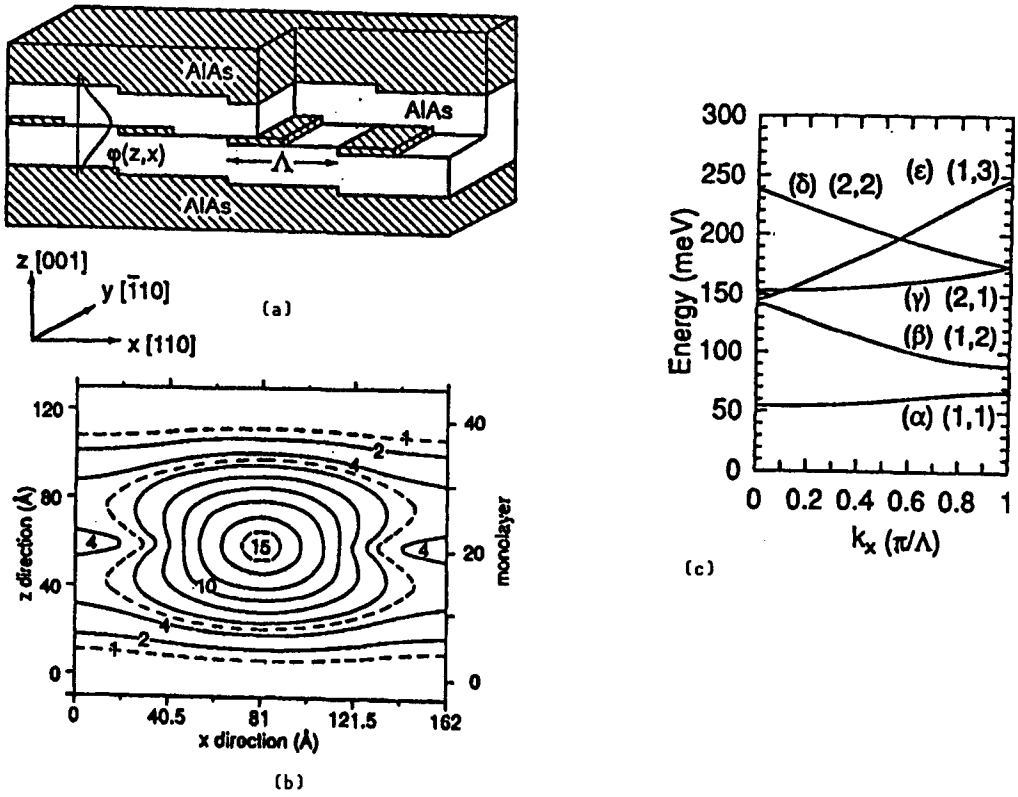

Figure 3. An Example of (a) Concept of Quantum Wire and a Surface Excess Using a Quantum Well With Inserted Grid, (b) Wave Function, and (c) Dispersion Relation
(The case of monatomic layer of the inserted AlAs layer.)

2.3 Design of Properties and Functions of Three-Dimensional Quantum Structures

In the structure where an AlAs grid is inserted periodically to the interior of an ordinary quantum well (Figure 3(a)), these grids are expected to behave as a surface excess quantum wire trains because the quantum wave of the two-dimensional electrons suffers from Bragg reflection. The wave function for the case when the thickness of the inserted AlAs is that of a monatomic layer is shown in Figure 3(b). An electron confining action is observable, but at the same time tunneling coupling between the neighboring wire is relatively strong, and it was found in the dispersion relation (Figure 3(c)) that the width of the miniband is about 10 meV. When the AlAs layer is five-atomic layer thick, the confinement is strong and it was found that the layer becomes almost an independent quantum wire.

The adsorption coefficient of a quantum wire or a quantum box becomes high at the absorption edge of light due to electron confinement so that it is attractive as a material for optical devices. From such a vantage point the following exploration was carried out this year: Namely, how much reduction in the absorption coefficient (that is, bleaching) can be achieved by the introduction of a certain number of electrons in a three-dimensional quantum

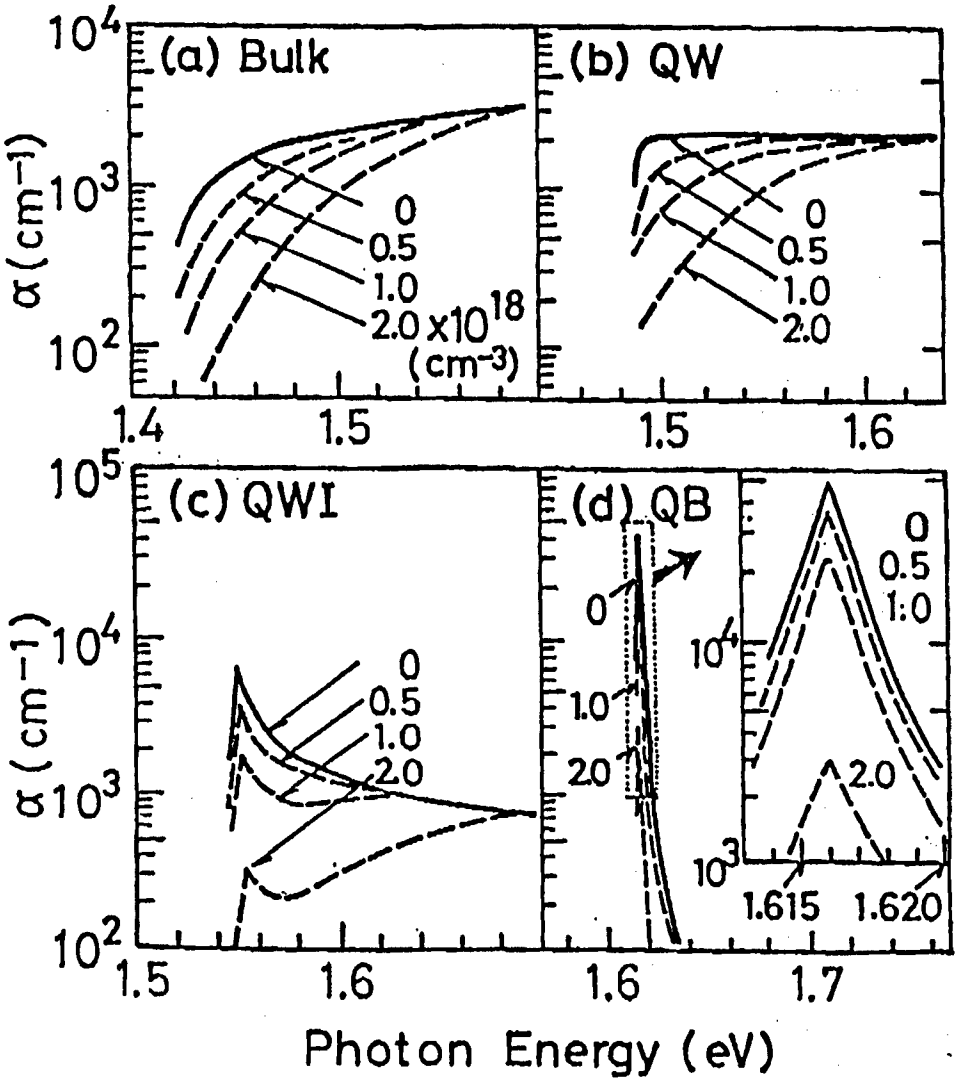

Figure 4. Optical Absorption Spectrum for (a) GaAs Bulk, (b) Quantum Well, (c) Quantum Wire, and (d) Quantum box, and the Manner of Reduction in Absorption Coefficient When Electrons Are Introduced to the Interior of Each (at room temperature 300 K))
(From APPL. PHYS. LETT., 24 December 1990.)

structure (Figure 4). As a result, it was discovered that in the quantum wire (c) or the quantum box (d) an improvement of several to several tens of times can be obtained over the bulk (a) or the quantum well (b). This has opened the possibility of application of new devices.

Atomic Layer Epitaxy for Creating Quantum Functional Structures

Akira Usui
Quantum Hyperstructure Group

A group III chloride is produced using a metal organic material and HCl, and a development of an metal organic chloride-atomic layer epitaxy (MOC-ALE) method was carried out by the use of a hot wall reaction tube. With this growth technique it became possible to grow a high purity GaAs ALE layer with a small amount of acceptor impurity mixing. By using this layer, a GaAs/GaP resonance tunnel diode structure was fabricated, and this confirmed the diode operation for the first time using the ALE method, though the data is preliminary. In addition, growth of this structure also on the sidewalls of the substrate crystal was attempted. These results may be viewed as amply demonstrating the possibility that this growth system can be applied to the growth of three-dimensional quantum wire and quantum box structures in the future from both the viewpoints of film thickness controllability and crystal quality.

1. Introduction

In order to realize quantum well structures or superlattice structures using semiconductor ultrathin films, a control of growth layers of atomic level is required, and at present, control in the unit of one molecular layer is becoming possible by the use of a molecular beam epitaxy (MBE) method or a metal organic vapor phase epitaxy (MOVPE) method. However, with these techniques, it is necessary to accurately control the partial pressure of supplied raw materials or flux: In particular, it is difficult to grow a uniform layer over a wide area of the wafer, selectively growing such a film, or to control the growth of a film to a substrate having structures.

Our group has been engaged in the research of a growth technique which makes it possible to form a three-dimensional quantum structure of compound semiconductor by the application of the ALE method. The ALE method, differing from the conventional growth technique, attempts to grow extremely accurately a film with thickness which is equal to the number of times of raw material supply multiplied by the thickness of one molecular layer as the unit, by alternately supplying the raw material gas containing the constituent elements onto the growth surface, and by means of the self-stopping function of the raw materials. The basic idea of the growth was proposed by Suntola in 1977. Subsequently, after GaAs epitaxial growth by use of group III organic metals was done by Nishizawa, et al., the method has been considered noteworthy as a growth means for ultrathin film growth with high controllability.

Our group has been pursuing the research on the chloride system ALE that uses chlorides of group III elements such as GaCl or InCl. This growth system enables one to obtain monomolecular layer growth for a wide range of growth

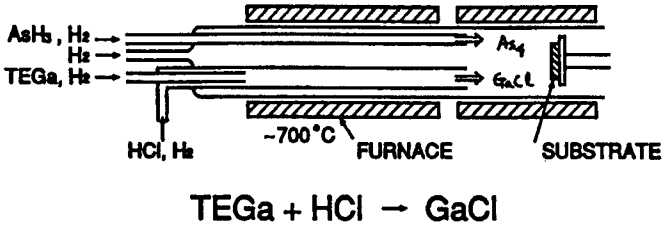

Figure 1. Schematic Diagram of MOC-ALE Growth

temperature and partial pressure of the raw material gas, in comparison to the MO-ALE method that uses group III organic raw materials such as trimethylgallium (TMG) or triethylgallium (TEG) that tends to be decomposed in the vicinity of the growth temperature. Moreover, there occurs no carbon contamination to the growth layer due to the organic raw material as seen in the MO-ALE method which leads to a significant feature that enables one to obtain a film with an excellent conductivity control. In the past, for the ALE growth, ALE process was carried out by moving a substrate, by using the multiple growth chamber reaction tube based on the hydride vapor phase growth reaction tube. However, because of the nuisance of substrate moving, and the necessity for group III metallic raw material, which is inconvenient to handle for chloride formation, and the difficulty in controlling the production of a chloride using HCl due to the dissolution of the chloride into the metallic raw material, a new technique called MO-chloride (MOC) method was developed in which chloride is produced by a group III organic material and HCl. In accordance with this technique the chloride ALE becomes possible without moving the substrate by the run-and-vent of the gas. Further, even if an organic raw material is used, growth with less carbon contamination can be expected because of the use of the hot wall. In what follows we will report on the result of evaluation of a GaAs film grown by the above-mentioned method and on the confirmed preliminary characteristics of a GaP/GaAs resonance tunnel diode structure that was fabricated.

2. Research Activities

2.1 GaAs ALE Growth by MOC Method[4]

In Figure 1 is shown a schematic diagram of the reaction tube for MOC-ALE growth developed this time. In the ALE growth of GaAs, triethylgallium (TEGa) is used as a group III organic material and is mixed with HCl on the upstream part of the reaction tube. When both gases are passed through the high temperature part of the reaction tube, GaCl is generated. On the other hand, AsH_3 was used as the material for arsenic, which is also decomposed when it passes through the high temperature part of the reaction tube, and most of it becomes As_4. These raw material gases are transported to the substrate part by the H_2 carrier gas. The growth was carried out under one atmospheric pressure of the reaction tube pressure. The conditions for the GaAs ALE growth are flow rate of 0.5 cc/min for TEGa and HCl, flow rate of 4 cc/min for AsH_3, flow rate of 5.6 ℓ/min for total H_2, temperature of 700°C for the reaction tube high temperature part, and the growth temperature of 450~500°C.

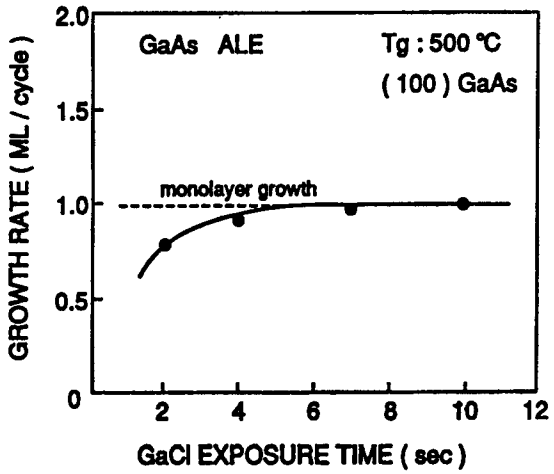

Figure 2. Relation Between GaCl Supply Time and Thickness of Grown Film in GaAs ALE

In Figure 2 is shown the growth rate (monolayer/cycle) as a function of the GaCl exposure time (t_{GaCl}). Here, the growth temperature was 500°C. The substrate used is GaAs (100). The growth rate was saturated when t_{GaCl} was about 5 seconds, and the film thickness per cycle had a value corresponding to the thickness of a GaAs monomolecular layer. Based on this result, t_{GaCl} was set at 5 seconds in the following experiment. The supply time of AsH_3 was also set at 5 seconds, the purge time of each raw material gas was set at 15 seconds, and one ALE cycle was carried out in 40 seconds. The above-mentioned purge time is a value determined from experiments because there the mutual mixing of the group III and the group V elements will not occur. At present, the inner diameter of the reaction tube has a large value of about 60ϕ, and a relatively large purge time is required because the growth is carried out under the ordinary pressure, but this time can be reduced by carrying out the growth at a low pressure.

2.2 Photoluminescence Evaluation of GaAs

In Figure 3 are shown the photoluminescence (PL) spectra at 4.2 K of GaAsALE layers grown at 450 and 480°C. The structure of the sample is what is obtained by continuously growing 11 layers of GaP as a cap layer on 1,060 layers (~3,000 Å) of GaAs. An isolated exciton emission in the vicinity of 8,180 Å and a DA emission in the vicinity of 8,330 Å were observed. In the growth at 480°C, the DA emission is decreased, and A^0X disappeared, also. The impurity corresponding to this acceptor level seems to be Zn. Further, the emission peak in the vicinity of 8,250 Å is considered to be an emission in which carriers that are accumulated in the interface between GaAs and GaP are involved from the fact that it is not observed when the GaP film on the surface is etched. From the above result, it was found that the principal impurity of the GaAs ALE layer formed by the MOC method is Zn, and C is hardly observed. Further, from the comparison of this result with MO-ALE with reduced diethylgallium-chloride by the use of a low pressure MOVPE system of local heating type by an RF pyle, a substantial reduction of DA emission was confirmed, in spite of the low temperature growth. This is considered to be

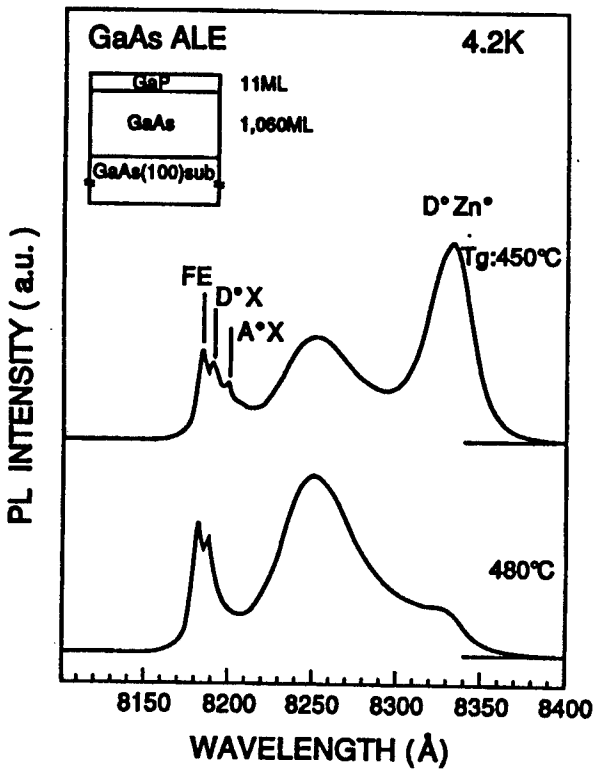

Figure 3. Photoluminescence Spectra of GaAs ALE Layers

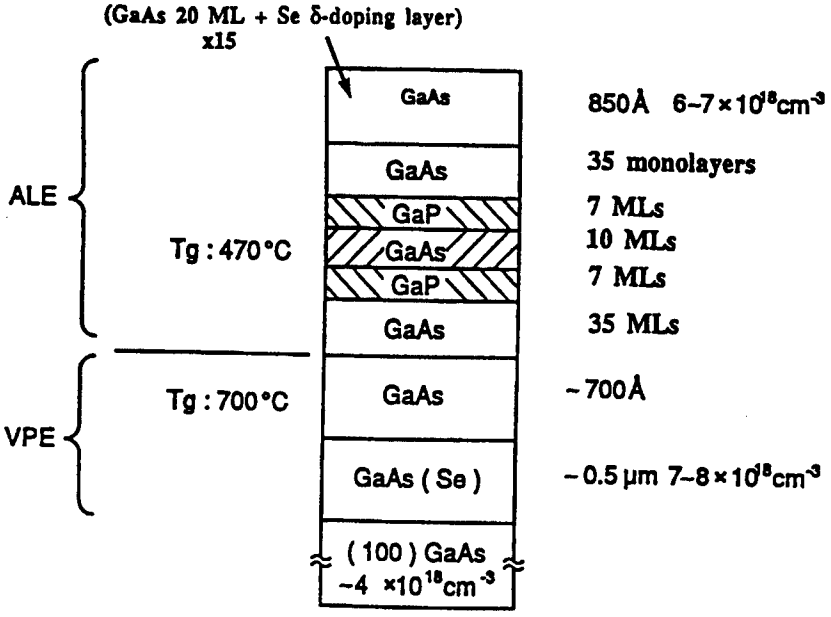

Figure 4. Growth Structure for GaP/GaAs Resonant-Tunnel Diode

due to accleration of decomposition of TEGa and the suppression of the generation of active radicals by the use of the hot wall type reaction tube.

2.3 Trial Manufacture of Resonant Tunnel Diode

On the basis of the feasibility of ALE growth of GaAs by the use of the MOC method, a resonance tunnel diode (RTD) structure consisting of GaP/GaAs as shown in Figure 4 was manufactured on a trial basis. Using n^+GaAs as a substrate, an 0.47 μm-thick GaAs buffer layer was deposited at 700°C by supplying GaCl and As_4 simultaneously on the substrate. Of the buffer layer about 700 Å is an undoped layer (background carrier concentration ~$10^{16}cm^{-3}$). Here, the temperature of the reaction tube was lowered to 400°C, and started ALE growth. After growing 35 layers (~100 Å) of a GaAs layer, a heterostructure of seven layers of GaP/11 layers of GaAs/seven layers of GaP was fabricated. Then 35 layers of GaAs layer were grown again. A 15 cycle structure was grown by finally inserting one layer of δ-doped layer of Se as a contact layer to 20 layers of GaAs. The carrier concentration of the contact layer under the conditions as determined by the hole measurement of a separate sample grown at a high resistance GaAs substrate, was 6~7 x $10^{18}cm^{-3}$. In this structure, the lattice constant (5.45 Å) of GaP is relatively small compared with the lattice constant (5.65 Å) of GaAs, with a mismatch of 3.5 percent, so that the film thickness available for coherent growth is about 100 Å. In this structure the total thickness of GaP is about 40 Å, and under these conditions, there is no room for dislocations to enter the crystal.

It is considered that the GaP lattice is deformed, being short in the growth direction. Figure 5 is a transmission electron microscope (TEM) image of the cross section of a sample having a similar structure. In this sample, 11 layers (30 Å) of GaP layer and 25 layers (70 Å) of GaAs layer were grown. The thicknesses of the grown films were nearly as planned, which showed the appropriateness of the ALE controllability. Although distinct heterostructures are observable, it can be said that fluctuations of the growth interface of GaP on GaAs seem to be greater than those of GaAs on GaP. The reason for this: The mixing of P and As of group V seems to be taking place, but the exact cause is not clearly known at present.

Using the above sample shown in Figure 4, an AuGe/Au electrode was evaporated on the surface through a 210 μm-thick metallic mask as shown in Figure 6(a), then a diode was manufactured by a mesa etching at room temperature using a mixed solution of H_2So_4:H_2O_2:H_2O = 1:3:5 with the metal as a mask. An In electrode was formed on the rear surface of the GaAs substrate. The I-V characteristic at room temperature is shown in Figure 6(b). The optimization of the growth conditions have so far not been carried out, and a detailed analysis of the diode including the improvement of the characteristic is planned to be executed in the future. It should be noted that RTD with the GaP/GaAs stress system is the first one, and RTD by ALE is also the first report of the kind.

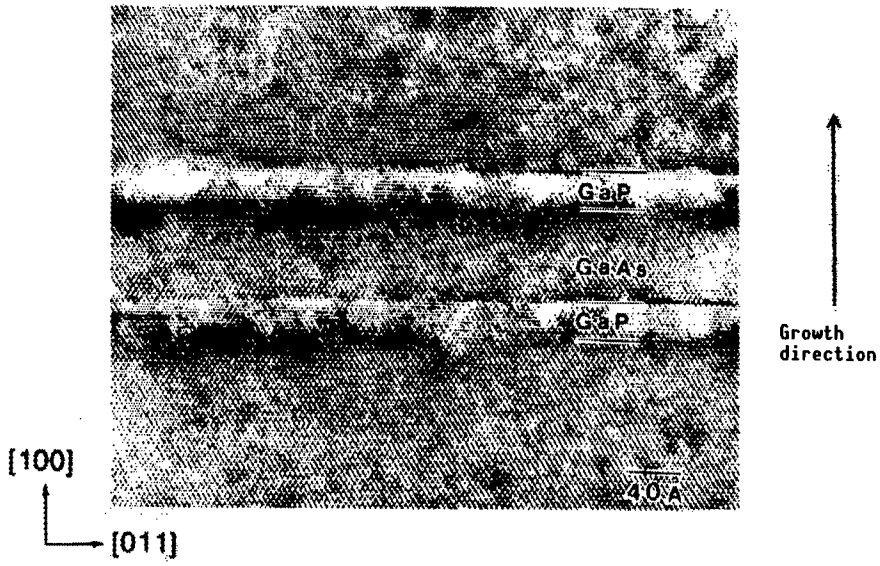

Figure 5. Sectional TEM Photograph of GaP/GaAs Resonant Tunnel Diode Structure

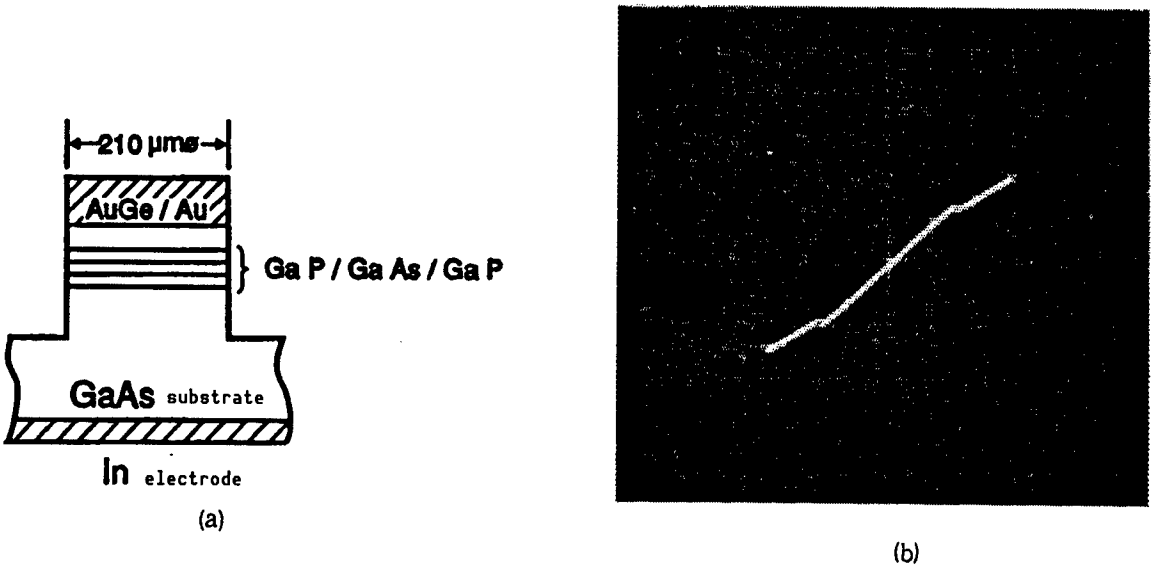

Figure 6. (a) GaP/GaAs Resonant Tunnel Diode Structure
(b) I-V Characteristic

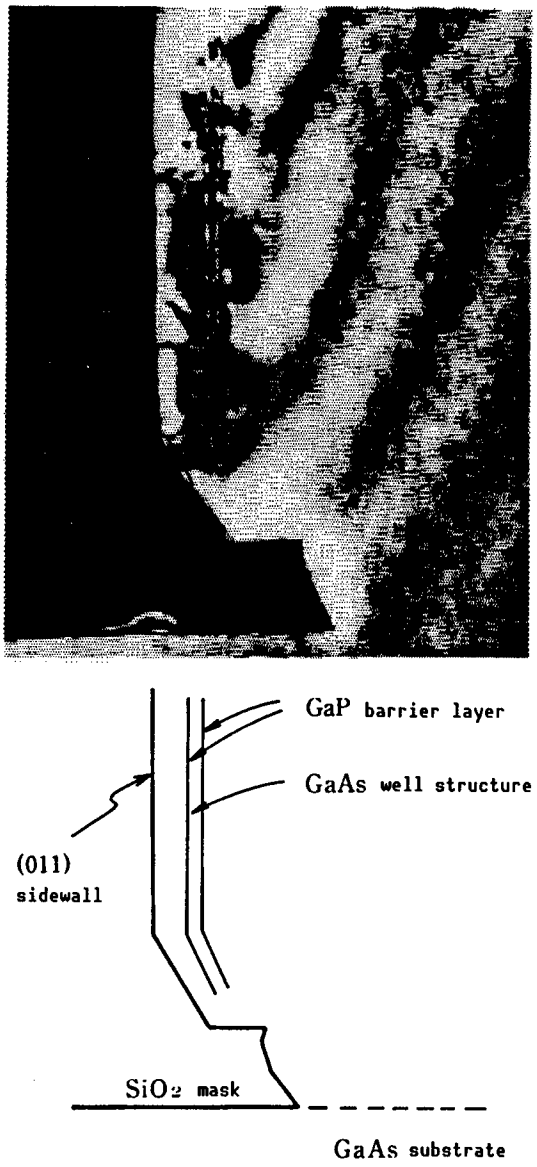

Figure 7. GaP/GaAs Resonant Tunnel Diode Structure Grown on (011) Sidewall

3. Future Development

As described in the above, metal organic raw materials were developed by the MOC-ALE method that is based on the formation of group III chlorides by HCl, and succeeded in the high-purity GaAs growth with small carbon contamination. Using this material, a GaAs/GaP resonant tunnel diode structure was prepared and the diode action was confirmed by the ALE for the first time, though the data just started to come in. This result shows that the growth system can positively be applied to the growth of the quantum wire and box structures in the future from both viewpoints of film thickness controllability of crystal quality. Further, although the detail is omitted here, the ordinary VPE growth

of InP and GaAs was tried by using this growth device, and the result revealed that the growth of very high purity with low ratio of V/III element ratio was achieved. For example, for InP a high value of μ_{77K} = 104,000 cm^2/Vs was obtained. These results also show that the present technique is an extremely effective technique for the reduction of carbon contamination.

Figure 7 shows a sectional TEM photograph of the RTD structure of GaP/GaAs grown on the (11) sidewall surface of GaAs. Recently, from the viewpoint of construction of quantum structures, epitaxial growth—not only on a flat substrate crystal but also on an irregular substrate with a structure such as this—is drawing attention. Since growth by this technique is determined basically by the thickness of the monomolecular layer of the growth surface and the number of the ALE cycles, the usefulness of the method in the field is extremely high. We intend to pursue the realization of three-dimensional quantum wire structures by the use of such a growth method.

Formation of Advanced Quantum Structures by the Overgrowth on the Edge of Quantum Well Structures

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Exploratory Device and Physics Group

The method of utilizing the edges of laminated ultrathin film is a powerful candidate for the formation of three-dimensional structures, especially quantum wire structures. The present article will describe, among several edge formation methods, the result of research in the molecular beam epitaxy (MBE) growth on the (111)A plane that becomes of concern in the etching regrowth method and the surface contamination by impurities. Further, as an alternative method of edge formation, the method of using the MBE growth on an inverted mesa will also be touched upon. In either method, the preliminary investigation is nearly completed, and it is in a stage of proceeding to the future formation of the three-dimensional quantum structures.

1. Introduction

As one of the powerful methods for the formation of the three-dimensional quantum structures, we have been examining the method of growing crystals on the edges of ultrathin laminated structures. The proposed methods of formation of edges that use the MBE growth may roughly be classified into three methods illustrated in Figure 1. Each of these methods has advantages and disadvantages, but the Exploratory Device and Physics Group has been engaged in the study of the methods (a) and (b). In method (a), a V groove is formed by chemical etching in a substrate that has a laminated thin film structure by MBE, and crystals are grown on the exposed edges (side faces of the V groove) of the ultrathin film structure. In the method (b), a laminated thin film is grown by MBE on a substrate that has an inverted trapezoidal pillar (mesa) and makes use of thin film edges that appear on the trapezoidal pillar. In the present article, in connection with method (a), it will be shown that a "selectively doped structure," that is required for the formation of the quantum wire structures on the (111)A planes which are the crystal surfaces that constitute the V groove side faces, can be formed by the MBE method. In addition, an ultrahigh vacuum through system, required for chemical etching and crystal regrowth, will be presented. In connection with method (b), examples of effective thin film edges obtained so far will be introduced.

2. Details of the Research

2.1 Utilization of Edges by Etching-Regrowth

The principal problems in the growth of crystals on the thin film edges exposed on the V groove side faces are: 1) that the side face of the V groove consists of a crystal plane, namely, (111)A plane, which is very different from the (100) plane that has been used in the conventional MBE growth, so

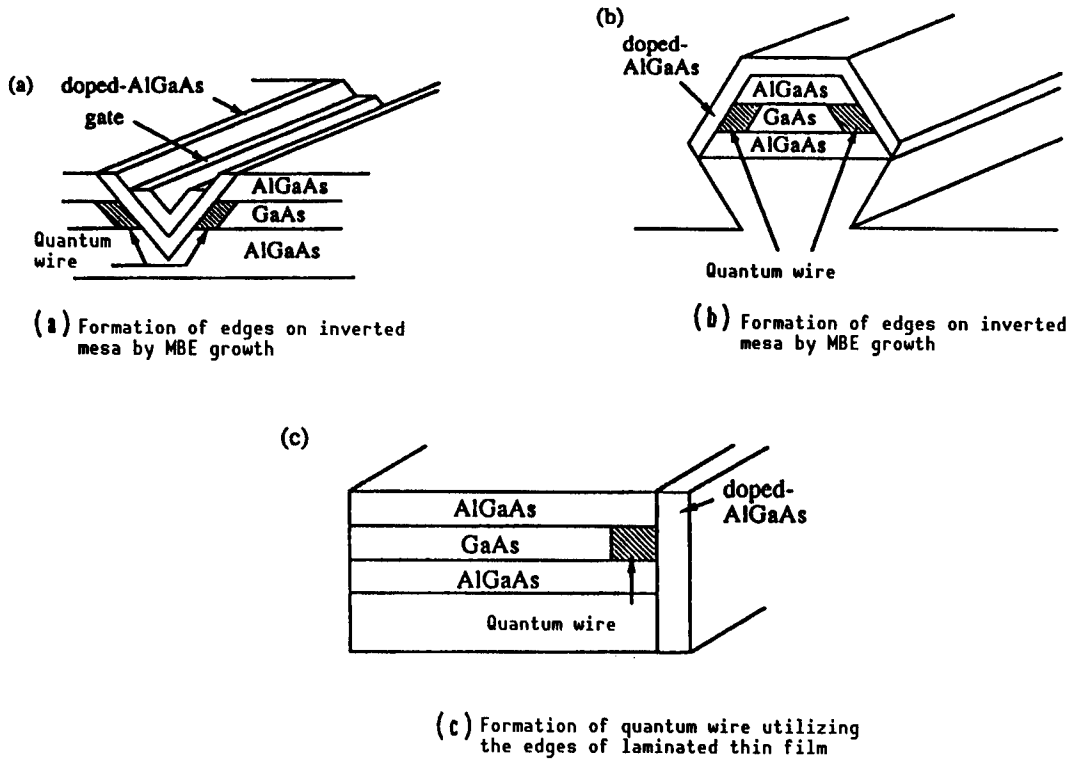


Figure 1. Formation of Quantum Wires Utilizing Edges of Laminated thin Film

that it becomes necessary to understand and control the crystal growth on this crystal plane, and 2) that the surface of the V groove is contaminated by impurities between the times of formation of the V groove and the execution of the crystal growth, so that it is difficult to obtain a satisfactory regrowth interface. The result of research on these points will be described in what follows.

2.1.1 Formation of Electrically Conductive Layer on (111)A Plane

One of the characteristics of the MBE growth on the (111)A plane is that when silicon (Si) is doped to form an electrically conductive layer, the electrical conductivity type becomes n-type or p-type depending upon the growth conditions. Accordingly, it is necessary to control both polarities in order to use it for the formation of quantum wires. We first obtained guides as to the control of electrical conductivity and crystallinity for a system which consists of simple gallium arsenide (GaAs). Next, as an index for evaluating the crystallinity in a concrete manner, we tried the formation of a "selectively doped structure" on the (111)A plane used for growth on the V groove.

The phenomenon that the Si-doped GaAs becomes n type or p type in the MBE growth on the (111)A plane is caused by the atomic arrangement of the (111)A plane. Figure 2 represents the atomic arrangement of the (111)A plane of GaAs.

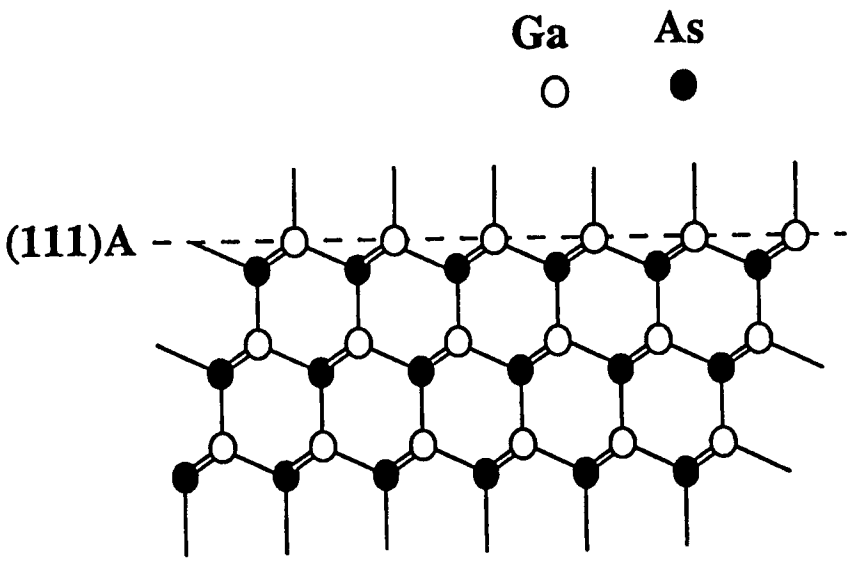


Figure 2. Surface Structure of (111)A Plane

The topmost surface is terminated in gallium (Ga) atoms, and at the time of crystal growth by the MBE method, arsenic (As) atoms which flowed in from the raw material cell are adsorbed to the Ga atoms on the topmost surface each with a single bonding arm. This adsorption with single bonding is weak and desorption of the As atom tends to occur. Now, if Si is applied at the same time for the purpose of forming an electrically conductive layer, Si may be bonded with As that is attracted or bonded with Ga from which As is attracted. When Si is bonded with Ga, the crystal becomes p type, and when it is bonded with As on the contrary, it becomes n type.

We tried to control the n type and the p type by varying the conditions of the MBE growth in order to change the density of As in the GaAs surface at the time of crystal growth. The result of the experiment is shown in Figure 3. In the figure, the abscissa, is the supplied As flux at the time of growth (represented by the equivalent pressure) and the ordinate (fA) is the rate of Si atoms bonded with Ga atoms. That $fA > 0.5$ means the p type, and $fA = 1.0$ represents the state in which all of the Si atoms are bonded with Si, whereas $fA < 0.5$ means the n type and $fA = 0.0$ represents the state in which all of the Si atoms are bonded with As atoms. From the figure it will be seen that by adjusting the supplied As flux (pressure) and the growth temperature of the substrate, it is possible to widely control the electrical conductivity type from an almost completely n-type state to an almost completely p-type state. That is, in order to obtain a p-type crystal, growth needs to be carried out at low As pressure and high substrate temperature, whereas to obtain an n-type crystal, growth needs to be carried out at high As pressure and low substrate temperature. In particular, in the case of high substrate temperature (580°C) and the case of low substrate temperature (480°C), the rate (fA) of Si bonding with Ga, namely, the electrical conductivity type, hardly changed even if the supplied As flux (pressure) fluctuates a little. This becomes significant in the actual fabrication of the device.

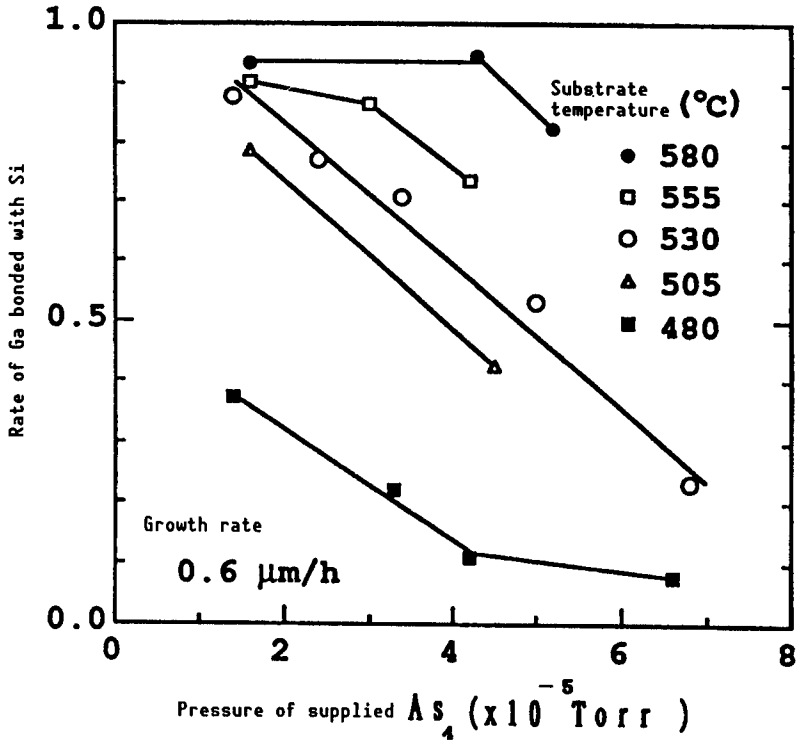


Figure 3. Control of Electrical Conductivity Type by Growth Conditions

As another parameter which affects the electrical conductivity type besides the As supply amount and the substrate temperature of growth, one may mention the flux of supplied Ga, and the relation between these crystal growth conditions and the crystallinity is also important. As a result of investigation on these points, for the case of obtaining high quality n-type GaAs crystal, in particular, it became clear that it is important to reduce the Ga flux and decrease the growth rate of the crystal. In addition, electrical conduction in the Si-doped GaAs and AlGaAs layers in the actual side faces of the V groove was also examined.

Next, based on these results, formation of a selectively doped (AlGa)As/GaAs structure are tried. The selectively doped structure is one in which an Si-doped (AlGa)As layer is laminated on a GaAs layer, and has a characteristic that there can be obtained a high mobility of holes and electrons. Figure 4 shows the temperature dependence of the surface density and the mobility of the holes in a p-type selectively doped structure, and Figure 5 shows the temperature dependence of the surface density and mobility of the electrons in an n-type selectively doped structure. Both Figures 4 and 5 show high values of mobility that are characteristic of selectively doped structures. Moreover, sufficiently high hole and electron densities are obtained, confirming that it is possible to form selectively doped n-type and p-type structures on the (111)A plane. In particular, the hole mobility of the p-type sample is a sufficiently high value for a p-type selectively doped structure and shows that serious problems in its crystallinity do not exist. On the other hand, the sample of the n-type selectively doped structure shown here is what was

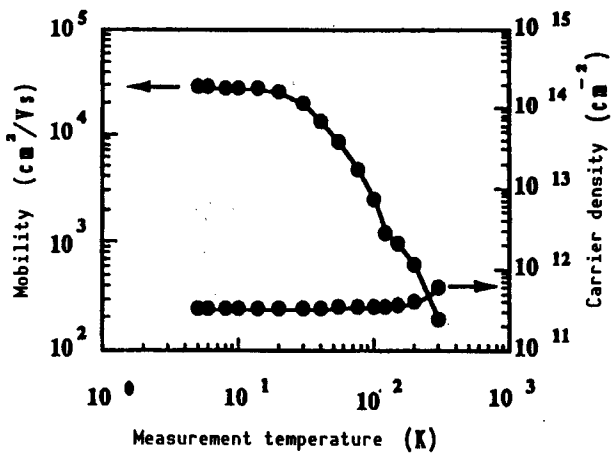


Figure 4. Temperature Dependence of Mobility of Two-Dimensional Holes, and Carrier Density in p-Type Selectively Doped Structure

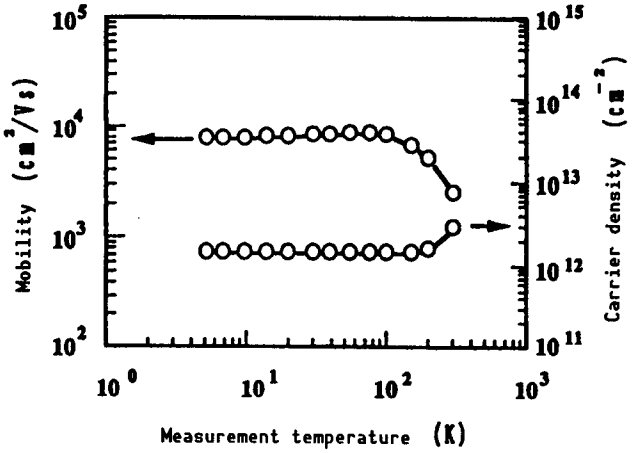


Figure 5. Temperature Dependence of Mobility of Two-Dimensional Electrons, and Carrier Density in n-Type Selectively Doped Structure

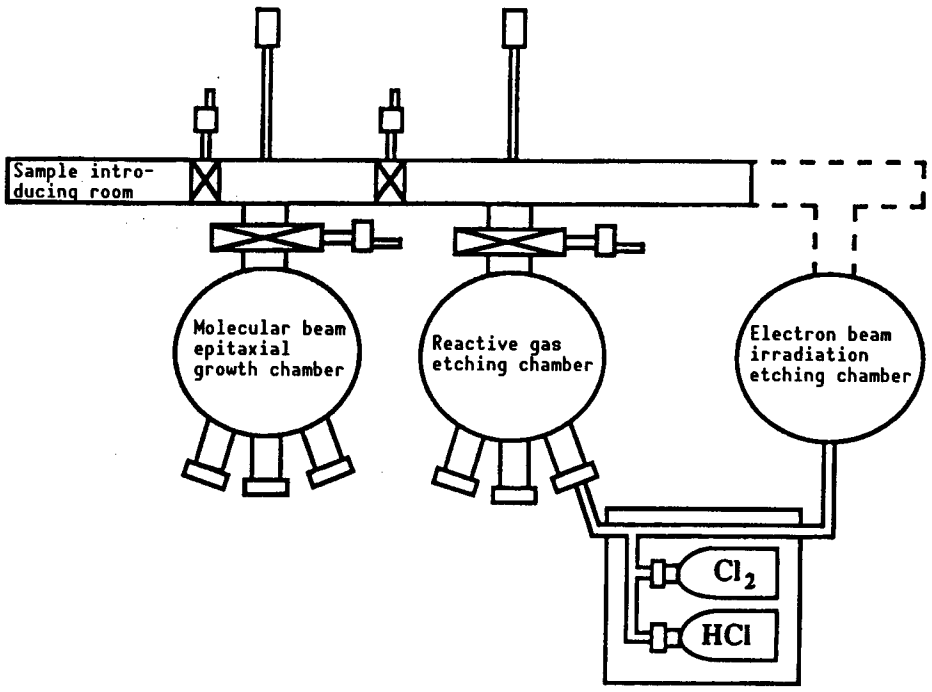


Figure 6. Ultrahigh Vacuum Through System

fabricated as a preliminary trial and no attempt has been made to optimize the structure and the growth conditions, so that the value for the electron mobility is not necessarily satisfactory value. It is, therefore, necessary to try in the future to optimize the structure and the like in order to improve the electron mobility.

2.1.2 Ultrahigh Vacuum Through System

In order to resolve the second problem (impurity contamination) in the formation of the quantum wire structure by the use of etching-regrowth, we introduced an ultrahigh vacuum through system as shown in Figure 6. The system has a structure that links a molecular beam epitaxy (MBE) growth apparatus and an ultrahigh vacuum gas etching apparatus with an ultrahigh vacuum transfer line, which enables crystal growth to start after the formation of thin film edges (V grooves) by reactive gas etching by the use of HCl, etc. This can be done without exposing the sample to the atmosphere and in a state where the surface of the sample is kept completely clean. The system is currently undergoing the starting-up and the function check and is expected to be put into operation shortly. Further, independent of this system, an electron beam irradiation etching apparatus is currently being started. This is a direct drawing etching system that employs electron beams, and drawing-etching-crystal growth of quantum wave structures in ultrahigh vacuum will become feasible in the future by linking the apparatus to the through system.

2.2 MBE Growth on Inverted Mesa

In the method which involves etching-crystal regrowth, a special system is required as described above. In contrast, the method which forms ultrathin film edges by the use of crystal growth on an inverted mesa (Figure 1(b)) has an advantage: The quantum wire structures can be formed by the use of ordinary MBE apparatus since a continuous crystal formation is possible. Figure 7 shows a sectional scanning electron microscope (SEM) photograph of a laminated thin film of GaAs and AlAs grown on an inverted mesa. A laminated thin film edge appears on the slope ((111)B plane) of the mesa. In the figure, crystal is growing slightly also on the edge, but the film thickness is very small, about 1/30 of the thickness of the top surface of the mesa ((100) plane). Therefore, a laminated thin film edge is already effectively formed. The reason for the appearance of a thin film edge on the mesa slope as in the above is due to a conspicuous presence of the difference in the properties of the growing crystal planes in a state where various kinds of crystal planes coexist. In the case of the structure described above, it is considered due to the migration of the raw material atoms from the (111)B plane (slope) to the (100) plane (the top surface).

3. Future Development

As described above, the formation of the quantum wire structures that utilizes the ultrathin film edges by etching-regrowth and the MBE growth on the inverted mesa, has nearly completed the preparation stage and is about to start the actual formation of the structures. The physical phenomena common to the two techniques described in the present article are the difference in the

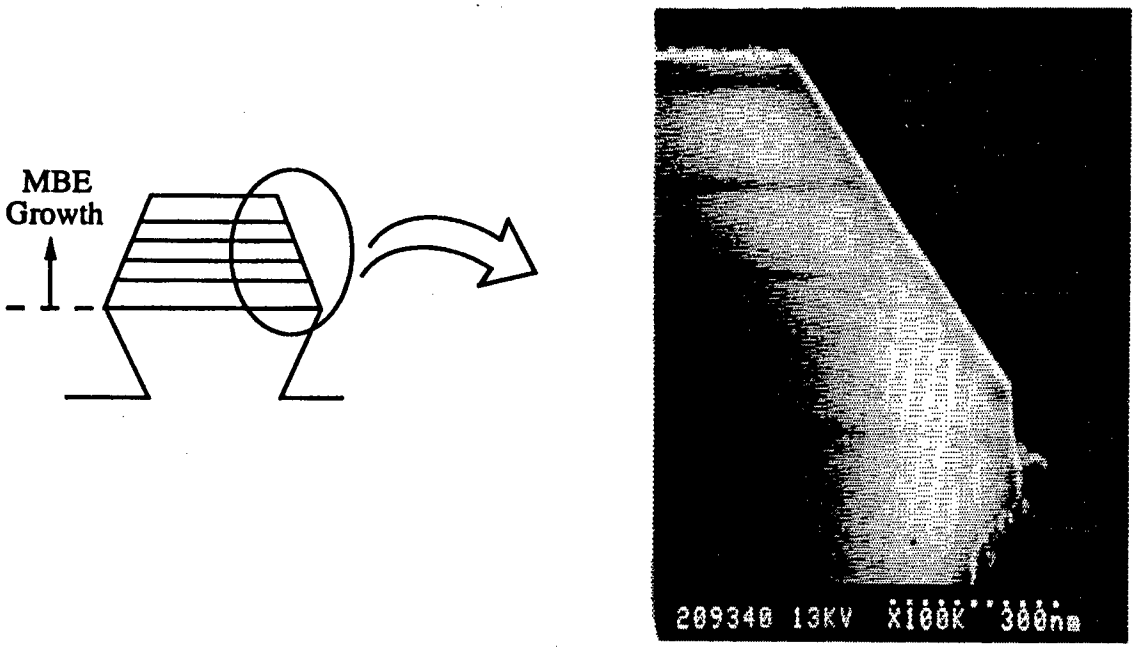


Figure 7. Sectional SEM Photograph of Laminated Thin Film Edge Structure by MBE Growth on Inverted Mesa

crystal growth properties in various kinds of crystal planes and the crystal growth mechanism when these various kinds of crystal planes coexist. These phenomena are essential for advancing the formation of three-dimensional quantum structures by crystal growth in the future, and it is necessary for us to obtain sufficient knowledge on the above-mentioned phenomena. Consequently, as a future development, we plan to pursue the following programs in parallel:

(1) Formation and physical property measurement of quantum wires by utilizing thin film edges.

(2) Evaluation of the difference in the properties of MBE growth by crystal planes and the elementary processes of the MBE growth when various kinds of crystal planes coexist.

Quantum Materials Having π-Conjugated Electronic System (Alkyl-Substituted Oligothiophenes): Properties and FET Operations

Shu Hotta
Quantum Hybrid Materials Group

In quantum microstructures using compound semiconductors, there appear various kinds of quantum effects which are utilized in various kinds of devices. One of the principal objects of the Quantum Hybrid Materials Group is to explore and elucidate quantum effects in materials system other than those mentioned in the above. From this viewpoint, in the research to be reported here we focused our attention to the electronics of the π-conjugated electronic systems in conductive organic materials and selected alkyl-substituted oligothiophenes as the model materials.

As a first step, we fabricated field effect transistors (FETs) which use these oligothiophene thin films in the channel parts, and evaluated their electric characteristics. As a result, it was confirmed in thin films made by using oligothiophenes substituted by alkyl group (or methyl group or ethyl group) that the mobility was sharply improved by about 10~700 times compared with the case of the samples that are not substituted.

1. Introduction

In the past, quantum microstructures were manufactured by mainly using covalently bonded materials such as compound semiconductors which manifested a variety of quantum effects. In the present research, aimed at the manifestation of the quantum effects in material systems other than those just mentioned, we design metallic materials or new organic materials that have π-conjugated electronic systems and explore the hybrid structure of these materials and the existing semiconductors.

Among others, organic materials having π-conjugated electronic systems exhibit interesting electronic properties as low-dimensional conductive bodies. For example, the π-conjugated electronic system of graphite shows the character of a two-dimensional electron gas, and is characterized by a high mobility of $10^3 cm^2/Vs$. In addition, there is reported an example of polyacetylene synthesis with high conductivity of $5 \times 10^5 S/cm$ which is comparable to that of copper or silver. Further, the π-conjugated electronic system can be understood approximately as an image of a free electron confined in a potential well. In this research we make active use of the π-conjugated electronic systems as material systems that have such quantum structures and aim at the research on the quantum effects that are exhibited by some of the hybrid structures of these materials with the existing semiconductors.

As an approach in such attempts, this research selected alkyl-substituted oligothiophene as organic materials having π-conjugated electronic systems,

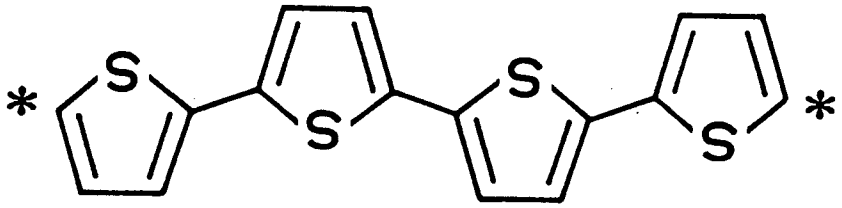


Figure 1. Molecular Structure of Oligothiophene

and the basic properties were measured and trial-manufactured FETs that use these materials in the channel parts and studied their operational characteristics.

2. Details of the Research

2.1 Physical Properties of Alkyl-Substituted Oligothiophenes

Oligothiophene is formed by linking several thiophene rings as shown in Figure 1, and has a structure in which the π-conjugated electronic system extends over the entire molecule. When the degree of polymerization is increased, the π-conjugated electronic system extends, and as a result the π-π^* transition energy is lowered (Table 1).

Table 1. Dependence of Absorption Peak Position of Oligothiophenes on the Degree of Polymerization

Species of oligothiophene	Degree of polymerization (n)	Absorption peak (π-π^*) (eV)
Bithiophene	2	5.04
Terthiophene	3	3.50
Quaterthiophene	4	3.18
Quinquethiophene	5	2.98
Sexithiophene	6	2.83

This suggests that the free electron model that extends over the entire oligothiophene is applicable, and it means that oligothiophenes with different degrees of polymerization are suitable as a model system for the quantum size effect. Further, through comparison with polymers of sufficiently large degree of polymerization (polythiophenes) it becomes possible to systematically discuss the electron structure as a function of the degree of polymerization.

These oligothiophenes form charge transfer complexes with acceptors such as $NOPF_6$ and TCNQ (tetracyanoquinodimethane). In this case electrons are transferred from the oligothiophenes to the acceptors. In such a state where

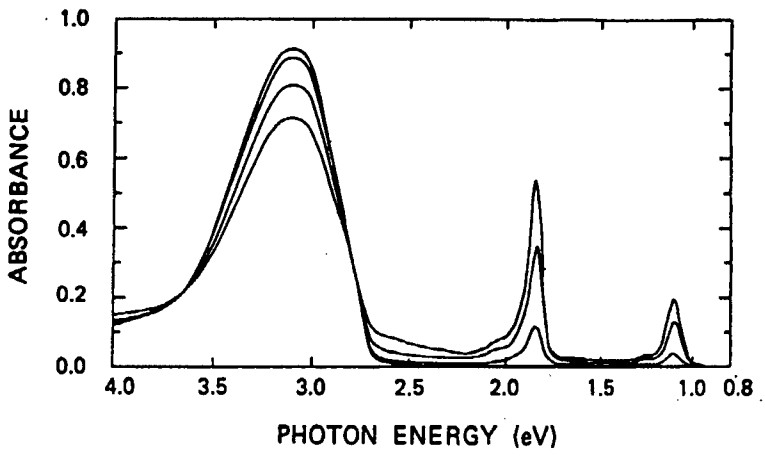


Figure 2. Spectrum Changes of Dimethylquaterthiophene Due to Doping

an oligothiophene is oxidized, the oligothiophene readily undergoes a chemical denaturation such as polymerization due to the high chemical activity of carbon atoms at both ends of the molecule (marked by * in Figure 1). As a result of synthesis and examination of various new materials by removing these disadvantages for the purpose of obtaining excellent model compounds, we found that oligothiophenes (with degree of polymerization of n = 3~5) in which the carbons on both ends are substituted by alkyl groups such as methyl group or ethyl group are especially suitable.

Figure 2 shows the change of the absorption spectrum of the solution in the chemical doping of dimethylquaterthiophene (a thiophene tetramer having methyl group on both ends) with $NOPF_6$. The doses of doping are 0, 25, 50, and 100 percent per thiophene ring. Dimethylquaterthiophene has an absorption peak based on the π–π^* transition in the vicinity of 3.1 eV, and the intensity of the peak decreases with the increase in the dosage. Along with it sharp absorption peaks characteristic of the doping species (oxidizing species) appear in the vicinity of 1.8 and 1.1 eV, and the absorption intensity of these peaks becomes large with the increase in the dose (amount of the carrier injection).

Such controllability of the amount of the carrier injection by a chemical doping of an oligothiophene can be considered in conjunction with the controllability of number of carriers by an electric field that uses the FET structure which constitutes a principal motivation of the present research.

2.2 FET Using Alkyl-Substituted Oligothiophene

An FET that uses an alkyl–substituted oligothiophene thin film as a channel material was fabricated according to the following procedure, and its operational characteristics were examined: Namely, an oxide film (270 nm) was formed on an n–type silicon substrate (δ = 0.01 Ωcm), and a source and a drain electrode were formed by evaporating successively chromium (15 nm) and gold (150 nm) on top of it (channel width of 1.5 mm and channel length of 4 μm).

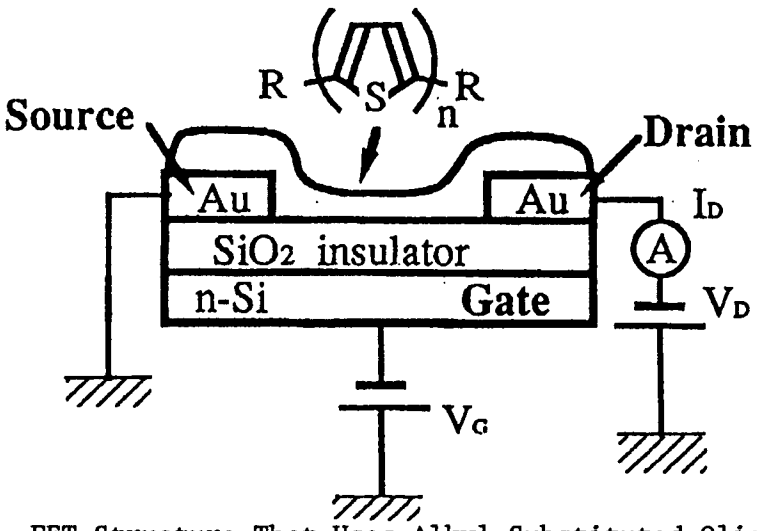


Figure 3. FET Structure That Uses Alkyl-Substituted Oligothiophene in Channel Part
(n is an integer from 3~5 and R is an alkyl group (methyl group or ethyl group))

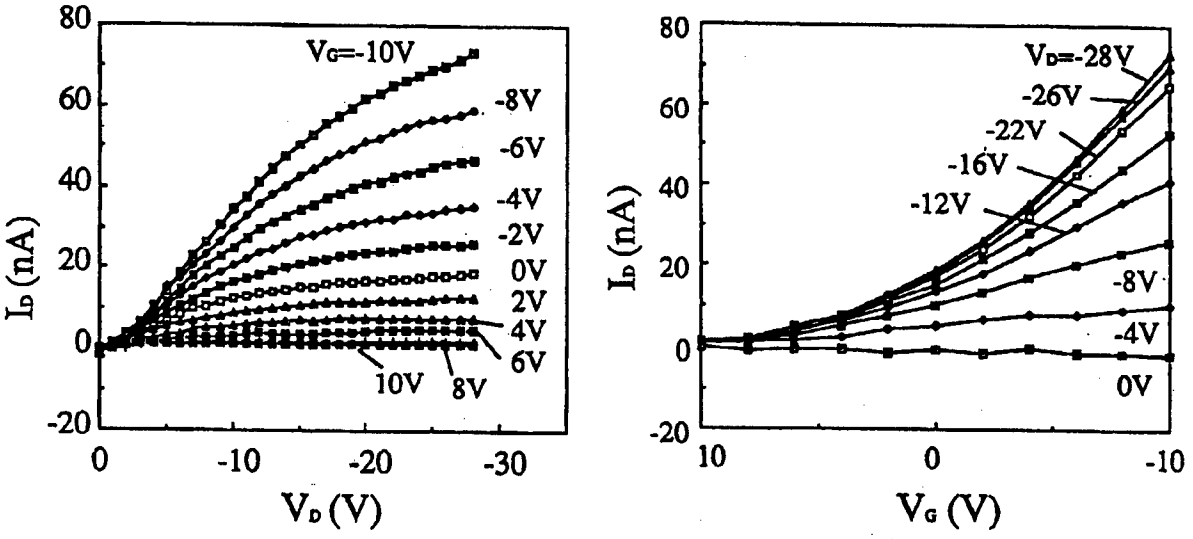
Next, an oligothiophene thin film was laminated between the source and drain electrodes on the silicon oxide film to form a channel, and the silicon substrate was used as the gate electrode (Figure 3).

An oligothiophene thin film can readily be formed by casting of solution or vacuum evaporation. In the former case, a chloroform solution obtained by dissolving diethylquaterthiophene (thiophene tetramer having ethyl group on both ends) at the rate of 1.5 mg/mℓ, for example, was cast in a nitrogen atmosphere to the channel part of the FET structure, and dried spontaneously at room temperature. In the latter case, oligothiophene was melted in a tungsten boat under a vacuum of 5×10^{-5} Torr, and an oligothiophene thin film with thickness of 100~500 nm was obtained by evaporating the sample for about 30 seconds.

In Figure 4 are shown the operational characteristics of an FET obtained by laminating a diethylquaterthiophene thin film by casting. From the fact that the drain current increases under application of a negative voltage to the gate, it was found that the carriers are the holes (Figure 4(a)). In addition, the mobility μ was evaluated from the following relation for the drain current (I_D) in the linear region (Figure 4(b)):

$$I_D = \mu C_0 \, W/L \, \{(V_G - V_T) \, V_D - V_D^2/2\}$$

In the equation, W is the channel width, L the channel length, C_0 the electrostatic capacitance of the oxide film per unit area, and V_G, V_D, and V_T the gate voltage, drain voltage, and threshold voltage, respectively. As a result, the mobility was estimated to be $5 \times 10^{-5} cm^2/Vs$. A similar FET operation was confirmed ($\mu \sim 9 \times 10^{-5} cm^2/Vs$) from an FET which has a laminated film evaporated in vacuum, and it was found that these values are about 200~400 times as large that of the case of unsubstituted quaterthiophenes.



a) Drain current-drain voltage characteristic

b) Drain current-gate voltage characteristic

Figure 4. Operational Characteristics of FET Using Diethylquaterthiophene

On the other hand, sharp diffraction peaks were observed in an X-ray diffraction experiment for both cases of cast film and evaporated film. The spacings are 19.4 and 19.9 Å for the cast and evaporated films, respectively, both being close to the value of 19.6 Å for the crystal, and this suggests that the film structure equivalent to that by the thin film forming methods is being obtained by other methods.

In addition, various alkyl-substituted oligothiophenes having different degree of polymerization (n = 3~5) and different substitution group (methyl group or ethyl group), other than diethylquaterthiophene, were similarly examined, and satisfactory FET operational characteristics were confirmed. The mobility of these oligothiophenes showed high values that are about 10~700 times that of the unsubstituted samples.

3. Future Development

The object of our study is to clarify the physical properties of organic materials as quantum structures of π-conjugated electronic systems by utilizing the FET structures. In order to examine the quantum effect it is considered that the study of the changes in the material characteristics as a result of control on the orientation and the arrangement, and the elucidation of the temperature dependence of the FET conduction characteristic seem to be the principal points. The Quantum Hybrid Materials Group is also aiming at the manufacture of laminated quantum structures of metals and semiconductors, and is examining the formation methods of hybrid structures of the GaAs/AlGaAs quantum structure and metallic materials.

Goto Quantum Magnetoflux Logic Project (1986-1991)
Supercomputers Through Superconductors

Eiichi Goto
Project Leader

1. Summary of the Project

The advancement of supercomputers is remarkable, and they are already being used for simulation of large-scale natural phenomena such as meteorology and for analysis of hyperfine phenomena or structures such as very large-scale integrated circuits (VLSIs), materials, and genes (DNAs). As a result, high-accuracy meteorological forecast, high-precision VLSI design, discovery of innovative materials became possible, contributing substantially to the advancement of mankind. However, in order to realize a truly practical large-scale and high-accuracy computer the operating speed of the existing computer has to be increased by several hundred times. The operating speed of the supercomputer has been increased within the past 20 years—since the first announcement of commercial equipment in the 1960s—at a rate of about 1,000 times. Accordingly, if one extrapolates this trend, one should expect the appearance at the beginning of the 21st century of an ultrahigh-speed supercomputer which can perform computations at a speed which is several tens to several hundreds of times faster than that of the existing machine; that is, at the speed of 100 billion to 1 trillion computations per second.

On the other hand, when one considers the signal transmission within the computer, during the time of one one-hundred-billionth of a second which is anticipated to be the operating cycle time of an ultrahigh-speed computer at the beginning of the 21st century, even light which has the fastest propagation time can propagate a distance of only 3 mm. Consequently, from the viewpoint of signal transmission distance, it is indispensable to shrink the dimension of the computer system to less than a cube with a size of several centimeters. To construct such an ultrahigh-speed and small-sized system using the existing semiconductor technologies is impossible from the viewpoint of the heat generation. Namely, the use of the existing bipolar semiconductors leads to an anticipation of the heat generation density that accompanies the miniaturization and increase in the operating speed to be comparable to that at the surface of the sun. Accordingly, appearance of devices with more superior characteristics is indispensable for the realization of ultrahigh-speed supercomputers that satisfy the speed requirement as mentioned in the above.

The quantum flux parametron (QFP) uses a fluxoid quantum as the unit of information so that it has the following three features. Therefore, it is expected to be a powerful candidate that overcomes the above-mentioned physical limitations.

(1) Low power consumption: Power consumption per logic gate of less than one one-billionth of a watt (one millionth of the existing ultrahigh-speed semiconductor).

(2) High-speed operation: Delay time per logic gate of less than one one-hundred-billionth of a second (one-tenth to one-hundredth of the existing ultrahigh-speed semiconductor).

(3) Magnetoflux coupling: Signal transmission by fluxoid quantum.

When items (1) and (2) are compared with the existing semiconductor device and the Josephson device, an especially significant feature is that the power consumption of the QFP is a small value of about one-millionth and one-thousandth of the values of the semiconductor and the Josephson devices, respectively. Because of this, there is no possibility of causing melting due to heat generation as seen in the silicon bipolar device, and the impossibility of cooling with liquid helium, which is the case for the conventional Josephson device, will not occur either. When QFP that has the above-mentioned features is employed, it will become possible to place an ultrahigh-speed supercomputer in a cube of a size smaller than several centimeters, so that an ultrahigh-speed operation which is faster by several tens to several hundreds of times that of the existing computer will become feasible. Therefore, QFP is promising for realization of an ultrahigh-speed supercomputer of the 21st century. The present project aims at the demonstration of the physical feasibility of each of the items that will be described below.

On the other hand, viewed from a different angle, QFP shows very interesting characteristics not only in the practical aspect but also in the theoretical aspect. Namely, when the operation of QFP is considered from the viewpoint of the information theory, it was possible to clarify that there exists a possibility that the Brillouin's negative entropy hypothesis, which is the grounds on which the conventional information theory is based, may not be valid. When we consider computations by QFP as a demonstration example, the observation of the following phenomena that are impossible to explain by the conventional theory can be expected. Namely,

(1) Possibility of operation at absolute zero where the entropy is zero (i.e., retention of entropy at absolute zero).

(2) Retention of information by an infinitely slow excitation (nongeneration of heat accompanying the disappearance of information).

Namely, the Shannon's information entropy and the Boltzmann's heat entropy, though each can be expressed by a simple relation, are not identical as has been thought in the past. Therefore, computations not accompanied by heat generation (generation of information) will become possible even without the use of reversible computation method.

2. Principal Activities of Various Research Groups

The Goto Quantum Magnetoflux Logic Project intends to demonstrate that the fundamental items that are necessary for realization of the ultrahigh-speed supercomputer of the 21st century are actually physically realizable. For that purpose, the research is being pursued by the following three groups.

(1) Fundamental Characteristics Group (in the Central Research Laboratories, Hitachi, Ltd.)

To elucidate fundamental physical phenomena of QFP devices and QFP circuits and to demonstrate the operational characteristics. The research is under way with the following as the main subjects.

1) Examination and demonstration of operational characteristics of the QFP circuits in the high-frequency region (above 5 billion Hz).
2) Design and demonstration of operational characteristics of highly functional and highly stabilized circuits.
3) Fundamental examination of three-dimensional mounting system by magnetic coupling.
4) Demonstration of magnetic flux detection devices with ultrahigh sensitivity.

(2) Construction Method Group (in the Central Research Laboratories, Hitachi, Ltd.)

To carry out research on the cyclic pipeline architecture (CPA) which makes active use of QFP circuits of the ultrahigh-speed clock cycle operation. In particular, research will be pursued with the following subjects as the centers.

1) Development of the kernel part which gives flexibility to the operating system.
2) To propose BL addressing which is a memory system suitable for CPA.
3) Verification by means of a computer (FLATS) for demonstration of CPA.

(3) Environmental Control Group (in Japan Vacuum Technology, Co.)

The research is aimed at the realization of an extra-fine magnetic field environment that insures the complete operation of QFP, and the technique for generating extremely low temperatures. The research centers around:

1) Examination of a micro heat flash method which detects the position of a magnetic flux that is trapped in a superconducting material and removes the magnetic field by locally heating the position with laser beams, etc.
2) Fundamental examination of ultra-small and high efficiency extremely low-temperature generation technique by means of a new cooling system.

Quantum Flux Parametron as a High-Speed Logic Device

Ryotaro Kamikawa
Fundamental Property Group

As the fundamental technology for putting the quantum flux parametron (QFP)—which is equipped with both the high-speed property and high-density mountability required as a circuit element for a high-speed computer—to practical use, a wide margin highly functional logic circuit D-gate was trial manufactured and its properties were evaluated, promising realization. Further,in a high-speed operation test by a one-half frequency division circuit, we succeeded in the operation at 8 GHz by reducing the excitation phase error by the standing wave method. We demonstrated the fundamental technology of interchip contactless signal which makes a high density three-dimensional mounting.

1. Introduction

The fundamental functions of QFP have already been demonstrated, and QFP is expected to be useful for making a supercomputer to have ultrahigh performance through its three-dimensional mounting based on its 1) high-speed performance, 2) low power consumption, and 3) magnetic flux coupling. Aimed at the practicalization of QFP, our group is engaged in the study of a high performance logic circuit system that uses QFP, fundamental technology for high-speed operation and fundamental technology for three-dimensional mounting.

2. Research Activities

2.1 QFP Logic Circuit System

The most fundamental circuit of QFP may be represented as shown in Figure 1. QFP operates in synchronism with a driving magnetic flux supplied externally to a driving line. A magnetic flux signal applied to the input line prior to the driving is output to the output line as an amplified signal by virtue of the physical properties of the superconducting loop that includes a Josephson junction when a driving signal is applied to the driving line. This fundamental unit corresponds, so to speak, to a transistor, and it is possible to construct a circuit that carries out a logical operation by combining the units.

Our group has been engaged in the research of such a logical circuit and a circuit system which we have succeeded in trial manufacturing is called a D-gate and has a structure as shown in Figure 2. In this circuit, x and y input signals are input to the input lines of QFPs, but s and t input signals drive two QFPs, and it has a feature in that signals (that is, outputs of other QFPs) drive the QFPs. In order to make this operation possible there is provided a partial circuit which realizes stabilization and amplification of driving magnetic fluxes.

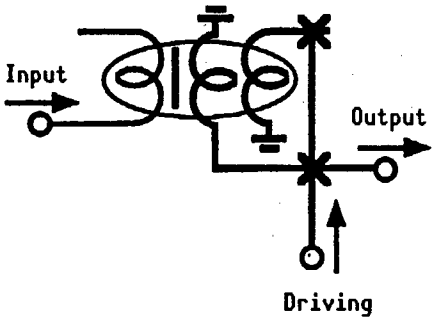


Figure 1. Basic QFP Circuit

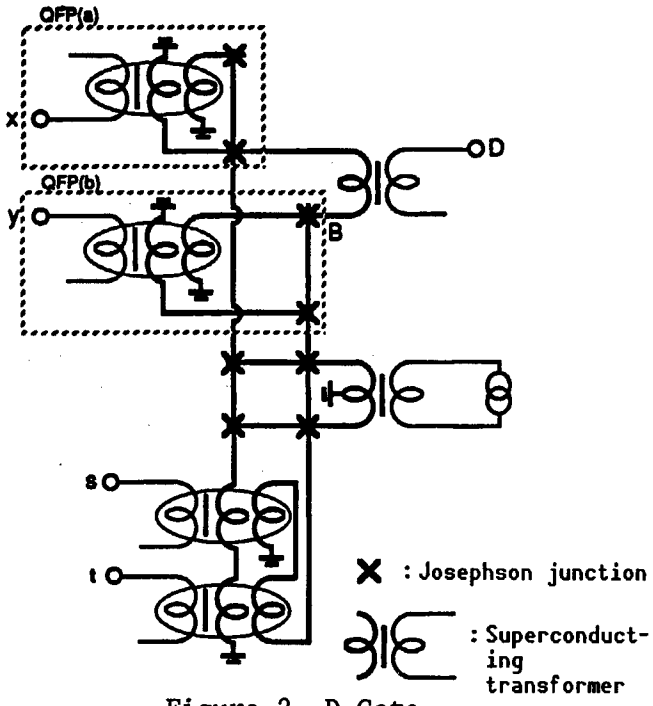
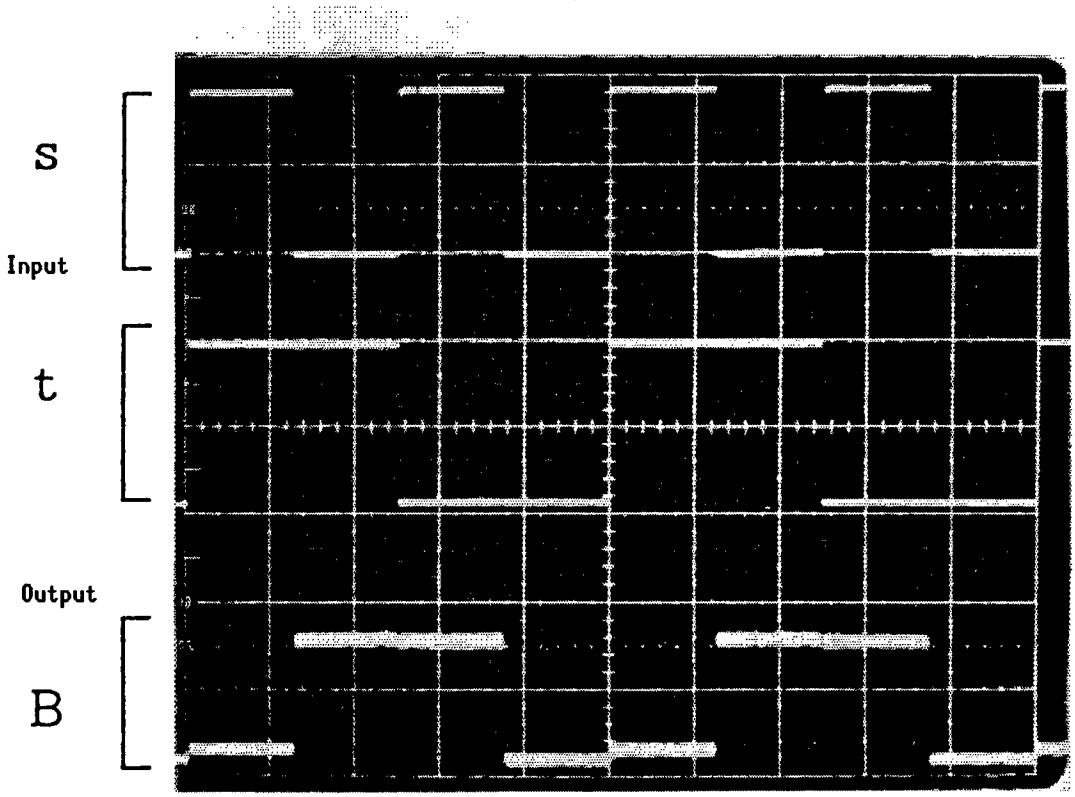


Figure 2. D-Gate

↓ Figure 3. Waveforms of Circuit Operation ↓



In the present trial manufacture we have confirmed the performance of this partial circuit. Figure 3 is an example of waveforms of circuit operation which shows the output at a point B when the input to y is fixed to unity and s and t are varied, and it can be seen that QFP(b) can be driven by the inputs to s and t.

This circuit has the characteristic that:

(1) A wide operational margin can be obtained even when there exists a nonuniformity in the properties of Josephson junctions, etc., and

(2) It has an excellent logical function and is possible to construct adders, etc., that are used in a computer in an efficient manner.

We are planning to confirm the overall circuit operation through trial operation based on the experimental data obtained this time.

2.2 Test of High-Speed Operation

Attempts to demonstrate the high-speed operation of QFP have been continued since the past, but the limitation to the operating speed originates from the technology for driving various circuits in synchronism and the technology of taking out feeble signals to room temperature systems by reducing the noise, rather than the performance of the circuit itself. Regarding the driving signal, the problem is the phase difference that is generated by a propagation of a signal at light speed between two circuits separated by several millimeters within a circuit chip. In order to solve this problem we developed a system (called standing wave method) which makes it possible to receive a signal to all points on a wiring by superposing on the same wiring mutually opposite driving signals by the use of reflection of the signal.

Further, in order to reduce the crosstalk noise induced the output line by external noise or input driving signals, we developed a package as shown in Figure 4 (a square pillar of outer dimension of 6 cm, and the circuit element is fitted to a 2.7 mm square part at the center of the circuit element). The circuit that was trial manufactured for testing was a frequency halving unit that generates a signal which is one-half of the frequency of the driving signal, and a high-speed operation at 8 GHz (four phases). This corresponds to a clock separation of 30 ps which is about two orders of magnitude faster compared with the existing fastest computer speed.

2.3 Fundamental Technology for Three-Dimensional Packaging

Since QFP transmits information by the use of a magnetic flux, it is possible to carry out signal transfer between circuit substrates in noncontact manner by stacking circuit substrates having circuits integrated in them, as shown in Figure 6. In addition, the power consumption of each of the substrates is extremely small (one millionth that of a semiconductor), so that the temperature rise due to heat generation will become of no concern even if a large number of circuit substrates are brought into close contact to each other.

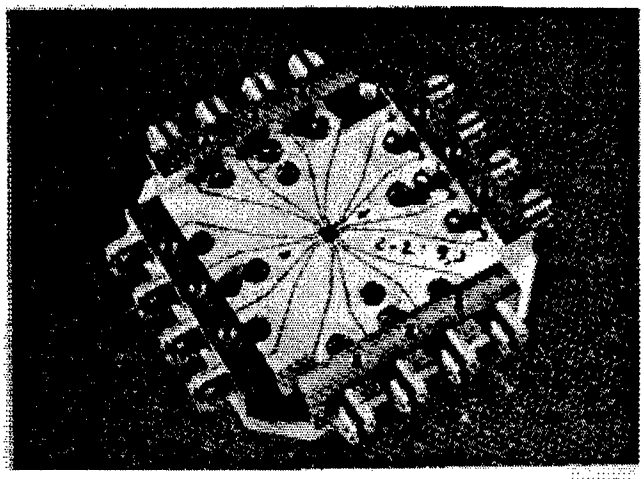


Figure 4. Package for High Frequency Measurement

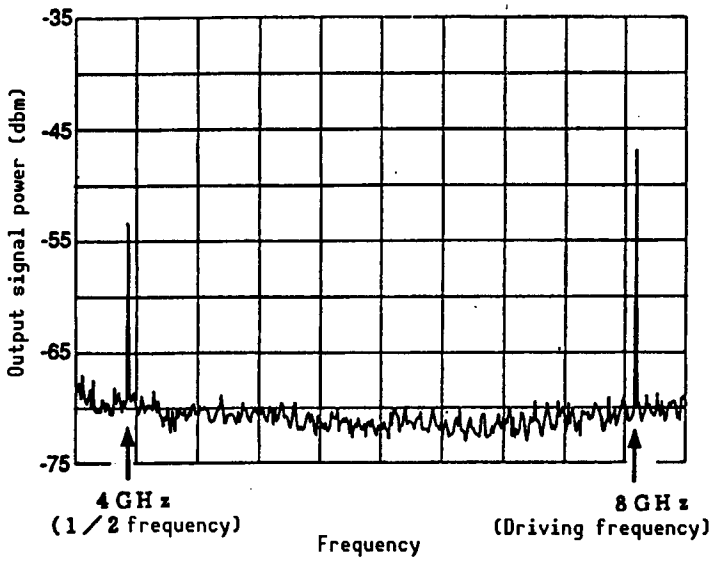


Figure 5. Frequency Analysis Result of High Frequency Operation

Then, it will become possible to house a CPU of a large-scale computer within a cube with a side of several centimeters.

As a first step toward demonstration for the feasibility of three-dimensional packaging, we trial manufactured a fundamental demonstrational model with a structure that has a chip mounted on a wiring board as shown in Figure 7. It should be pointed out that Figure 7 shows the mounting of a wiring board with a chip within a ceramic package. In this demonstration model, QFP is provided on the chip, a driving line for driving the QFP and signal lines connecting the chips are provided on the wiring board, and the chip and the wiring board are connected in noncontact fashion by the transcoupling.

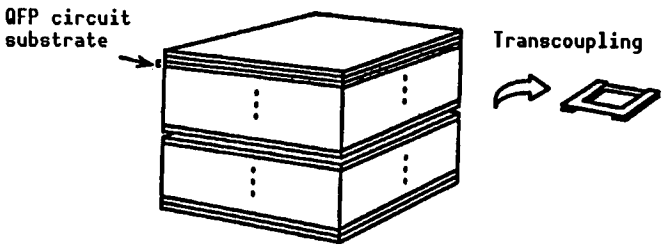


Figure 6. Three-Dimensional Packaging of QFP

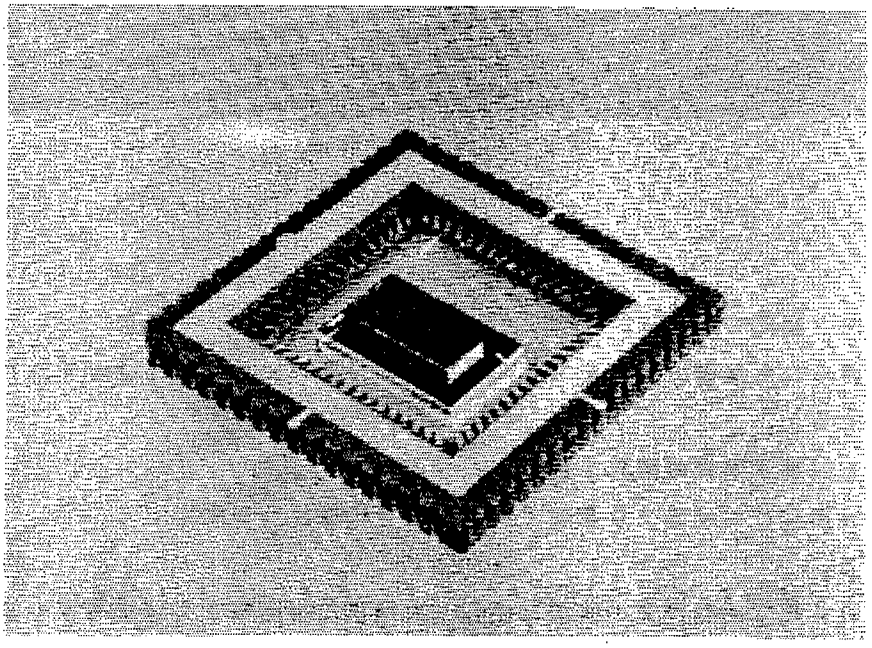


Figure 7. Demonstrational Model for Fundamental Three-Dimensional Packaging

Since the chip and the wiring board need to be laminated with high positional accuracy, the alignment error was suppressed to about 3 μm by the use of an aligner (Figure 8 [not reproduced]) for a chip specially designed and manufactured.

Using this sample we succeeded in a fundamental experiment for operating the QFP element on the chip with an input signal from the wiring board.

3. Future Development

During the course of the present project, we are planning to carry out the following:

(1) To confirm the high-speed characteristics of the wide margin and highly functional logic circuit D-gate based on the fundamental data already obtained.

(2) To determine more accurately the limits of the ultrahigh-speed driving by continuing the existing effort.

(3) To develop more advanced noncontact signal transmission technology in three-dimensional packaging.

As an extension of the confirmation of these fundamental properties, we have a high expectation for the practicalization of circuit elements for supercomputers, which will replace the silicon technology that is anticipated to encounter a limitation at the beginning of the 21st century, by resolving design problems such as noise that occurs in the realization of large-scale circuit systems, manufacturing problems such as the nonuniformity of the characteristics, high frequency multiphase driving method, etc.

Evaluation of a Cyclic Pipeline Computer, FLATS 2

Mitsuhisa Sato
Computer Architecture Group

A computer, FLATS 2, which is obtained by applying the cyclic pipeline architecture (CPA) system proposed as a suitable system for computers that use a quantum magnetic flux circuit, was trial manufactured and operating systems and compilers were developed and evaluated. The CPA system is a system for executing a plurality of programs in parallel with a pipeline system, but two programs are executed in parallel with FLATS 2. As a result, in a LINPACK benchmark that is made parallel, it was possible to obtain performance which is better by 1.8 fold by placing it to two parallel programs. Further, in FLATS 2 the execution of individual programs can be improved by about 20 percent by enhancing the instruction to be highly functional through the use of BL addressing mechanism obtained by adding the range inspecting function to memory addressing.

1. Introduction

A program that is given to the computer is stored in a memory as a sequence of many instructions, and various processings ranging from scientific and engineering computations to business computations are carried out by interpreting and executing these instructions. The performance of a computer is determined by how efficiently these instructions are executed.

Execution of an instruction may be divided into stages of fetching of the instruction (IF), decoding of the instruction (ID), and execution of the instruction (EX). The pipeline system is aimed at processing a continuous plurality of instructions in parallel by decomposing instructions into stages and executing them as if in a flow system (Figure 1).

When a computer is constructed using new logic elements, it is necessary to have a constitution which makes active use of the characteristics of the elements. In the logic circuit the quantum flux parametron (QFP), each element has its internal states, and the system is operated by causing transitions of states by control signals (clocks). Therefore, a computer that uses QFPs becomes a computer which has a very large number of stages that have the individual logic element as the stages by the pipeline system. In contrast, the number of pipeline stages in the existing elements does not amount to much because they require circuits for holding the internal states.

In general, according to the pipeline system, it is possible to increase the processing speed N fold by subdividing the instructions into N stages. However, in an actual program, instructions cannot be executed in parallel according to the pipeline system when execution of a new instruction has to use the result of instruction previously executed, such as in the case of

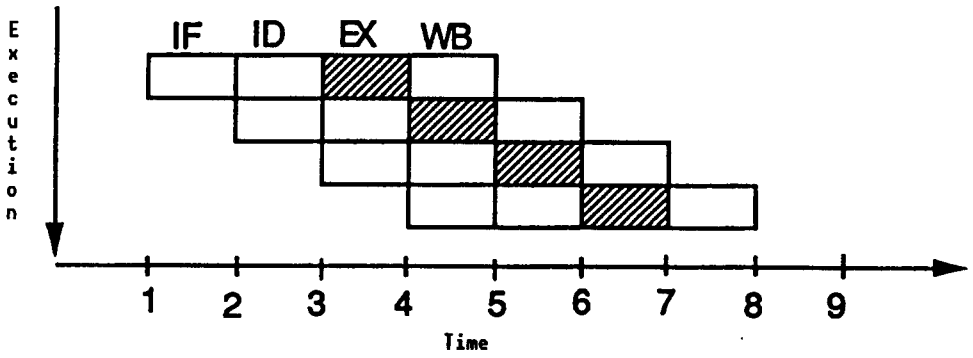


Figure 1. Pipeline System

controlled branch instructions. Because of the presence of such a dependency relationship between instructions, it is not possible to attain a high efficiency that can be expected for a QFP computer by the high degree of pipelining.

The cyclic pipeline architecture (CPA) is one aimed at executing a plurality of programs according to the pipeline system. When there is a pipeline of N stages, instructions of N different programs are executed in sequence. When one considers a program, an instruction is executed for each of the N stages so that the preceding instruction is completed at the time of execution of the next instruction. Assuming that there exists no dependency relationship between different programs, the efficiency will not be dropped even if there exists a dependency relationship between the instructions within one program. Hence, CPA may be said to be a system which is suitable for the QFP computer which is pipelined to a high degree.

The CPA is a system which enhances the overall processing capability by processing many programs in parallel in exchange for the fast execution of the individual programs. At present research is in progress on the parallelization in which one problem is solved by executing a plurality of programs in parallel, in the field of scientific and engineering computations, etc. Moreover, even a program according to the conventional classification can be made to be executed at high speed according to the CPA system by rendering it parallel.

As a precursor to the QFP computer, we developed a computer, FLATS 2, according to CPA using existing silicon elements, studying the effectiveness of CPA. As a result, it was found that CPA is effective not only for the QFP computer but also for the computer that uses the existing elements.

2. Research Activities

2.1 Evaluation of BL Addressing

The BL addressing is a mechanism which is obtained by adding the range inspecting and branch controlling functions to memory addressing proposed for and mounted on FLATS 2. In a repetitive operation of a frequently appearing

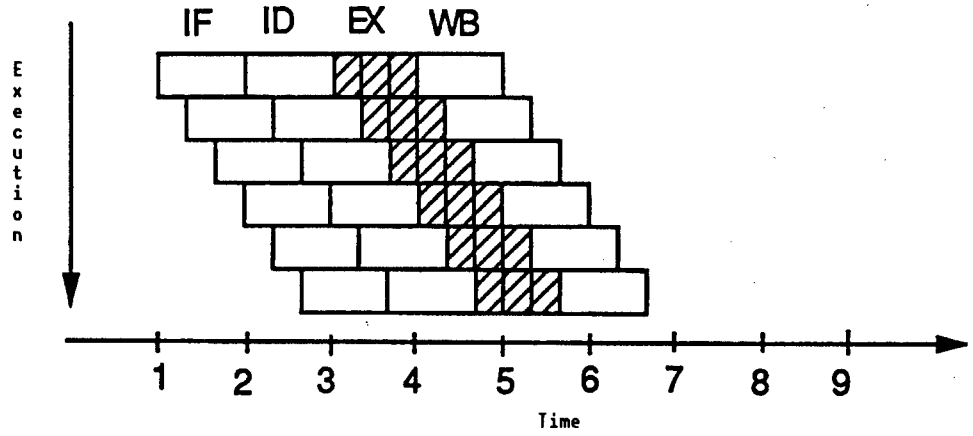


Figure 2. Pipeline With Large Stage Number

arrangement in numerical computations, it is possible by the use of the BL addressing to carry out by a single instruction the fetching and operation of a memory operand, judging and branching of updating and completion of the address to be accessed next. In an instruction of the conventional computer these operations will have to be carried out in several instructions. The CPA is a system which is aimed at increasing the efficiency by processing the instructions of a plurality of programs by parallel processing, but the processing speed can further be increased by rendering the individual instruction highly functional by the BL addressing.

We developed a FORTRAN compiler which automatically applies BL addressing to the operation of a repeated arrangement. By the application of BL addressing it was possible to obtain a performance magnetic resistance of 1.3 fold for the LINPACK benchmark in the solution of a set of simultaneous linear equations according to the Gauss' elimination method, and a means of about 1.2 fold for the LIVERMORE benchmark for evaluating the performance of the loop used for numerical computations.

As to the BL addressing, there are proposed applications not only to numerical computations but also to the increase of the data type inspection at the time of execution of the LISP language and the detection of an invalid pointer for a C language, etc.

2.2 Evaluation of FLATS 2 System and Parallel Programming

The FLATS 2 can process two programs in parallel by the CPA system. From the programming viewpoint, this is equivalent to having two processors so that it is not possible to use the conventional one with one processor as the operating system for controlling the execution of the computer.

Under these conditions, we developed an operating system, CPX, for the parallel computer. The CPX adopts an object-oriented concept in order to be able to execute in parallel the processing itself of the operating system.

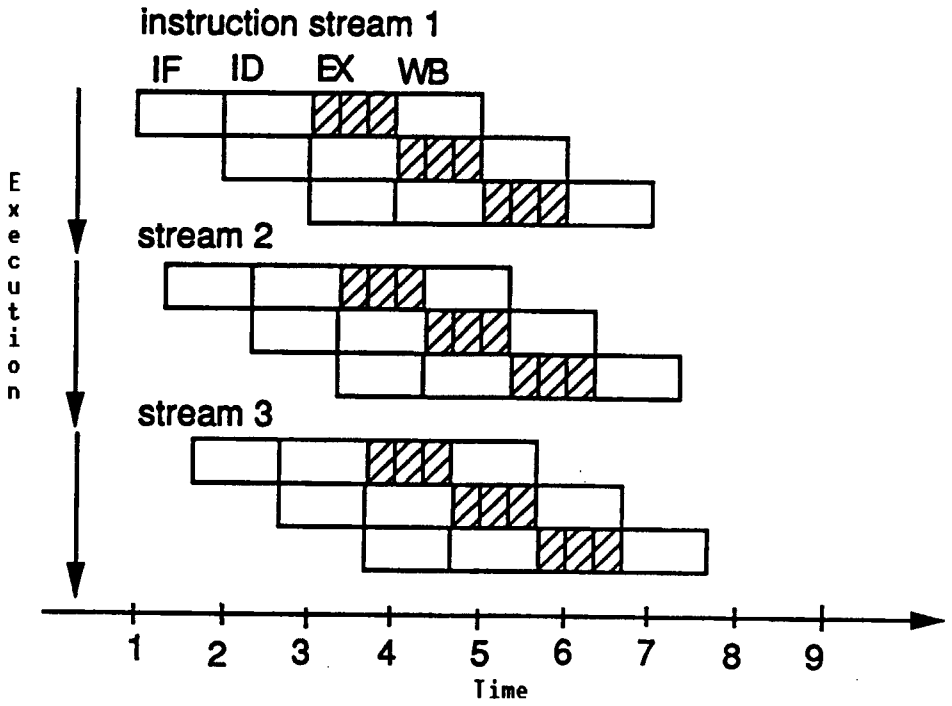


Figure 3. Cyclic Pipeline System

Further, FORTRAN was extended to permit it to describe parallel programs and that function was taken into the compiler.

The evaluation of the trial manufactured apparatus was such that for the case of using one processor alone, the performance of the LINPACK benchmark that was used along with the FORTRAN compiler is 2.6 MFLOPS. When the programs of simultaneous linear equations of the Gauss' elimination method are rendered parallel by the parallel FORTRAN compiler and executed using two processors, the performance was 5.0 MFLOPS which is 1.8 times that of the case of single processor.

2.3 Evaluation of CPA by Model

The QFP computer is considered to have a larger stage number of pipelines than that of FLATS 2. We carried out an experiment for the case when the number of stages is large by using a simulator that was developed for FLATS 2.

In Figures 2 and 3 there are shown the situation in which instructions are executed by the pipeline system (superpipelined system) with large stage number of programs which is one of the conventional systems, and by the pipeline (cyclic pipeline) of the CPA system. Figure 4 shows the improvement of the performance in the LINPACK benchmark. As the number of stages of pipeline increases, in the conventional pipeline the performance improvement is saturated due to the presence of a dependency relationship between instructions. In contrast, in the CPA system it is possible to realize a performance improvement which is nearly proportional to the stage number. The LINPACK program is an example where the parallelization is relatively easy, and the

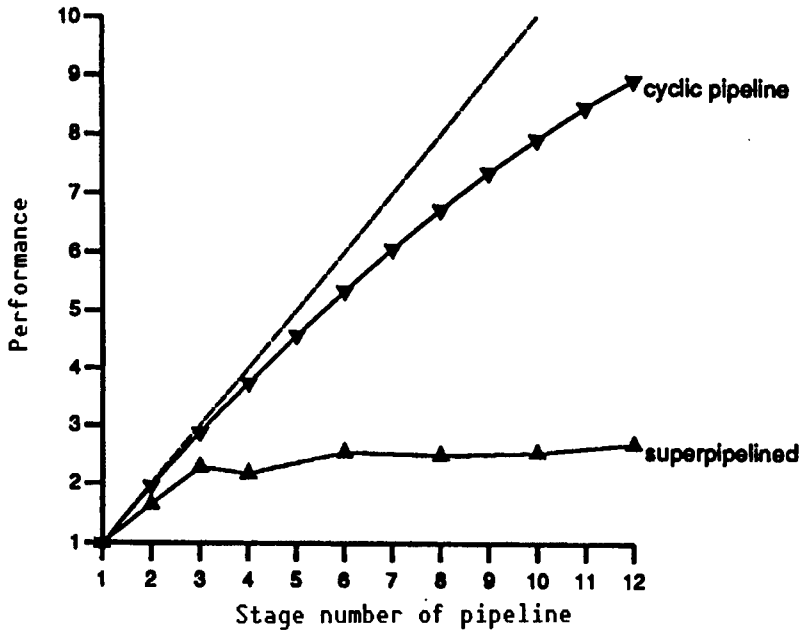


Figure 4. Comparison of Pipeline Systems

effect of the CPA system is large. It should be mentioned that not all programs can be rendered parallel, but many of the scientific or engineering computations permit parallelization so that an increase in the efficiency due to CPA system can be expected.

3. Future Development

The CPA system is a system which effectively utilizes the pipeline with large number of stages through parallelization, and its effect was confirmed also in FLATS 2 that uses the existing elements. This system seems to be an effective system for the QFP computer where the stage number is still larger. In order to obtain a large effect by the CPA system it is necessary to render the programs parallel so that the research on the automatic parallelization of programs and the parallel algorithms will become important.

Detection of Trapped Flux Quantum in Superconductors

Junpei Yuyama
Magnetic Shield Group

A new method for detecting a flux quantum trapped in a superconductor was developed. The method is to scan a detection coil parallel to the surface of the superconductor close to the superconductor, and a low sensitivity to an external magnetic disturbance and a high sensitivity to a flux trapped are made compatible. In order to keep the height of the coil constant, a gas floating method was developed. It was confirmed experimentally that it is possible to keep the height of the detection coil constant in the gas floating method, and that the sensitivity for the flux measurement is sufficient for the detection of an isolated single flux quantum.

1. Introduction

Our group has been engaged in the technologies for generating ultralow magnetic field and extremely low temperatures that are important as the operating environment for the quantum flux parametron (QFP). Here, we will report on the generation technology of ultralow magnetic fields, in particular, on the research about the detection technology of trapped flux quanta, which plays an important role in the ultralow magnetic field generation technology.

The research on the technology of ultralow magnetic field generation has been pushed in two directions. The first direction is to establish a technology for excluding a flux trapped in a semiconductor. An external magnetic field is almost completely excluded in principle from the interior of a magnetic shielding vessel made of a superconductor. In reality, however, there occurs a phenomenon that a flux remains trapped in the wall of the superconductor vessel so that a complete exclusion of the external magnetic field is not accomplished. Under these circumstances, we devised a method (micro heat flushing method) by which a trapped flux is excluded by sweeping with a normally conducting hot spot, and we are trying to establish the method. For the confirmation of sweeping and exclusion of a trapped flux, it is necessary to detect whether there exists a trapped flux and its position. The trapping of fluxes occur with an extremely small flux quantity of a flux quantum (2.07×10^{-11} Wb which is about one 1.5 millionth of the flux due to geomagnetism that penetrate through the area of 1 cm^2) as a unit, so that it becomes necessary to have a highly sensitive flux detection means that can handle the situation. The second direction is to clarify the conditions on the shape and dimension of the superconductor for suppressing the generation of flux trapping on the magnitude of the residual magnetic field, etc. A superconducting electronic circuit is formed on a superconductor called a ground plane via an insulating film. When a flux is trapped in the ground plane, various defects arise in the circuit operation. Therefore, it becomes necessary to search for a method which will reduce the residual magnetic field to the maximum extent

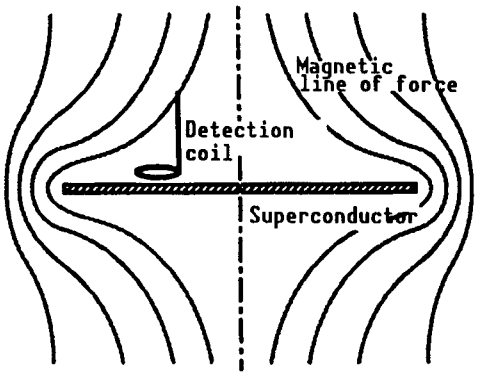


Figure 1. Magnetic Lines of Force of External Magnetic Field Will Not Pass Through the Direction Detection Coil of Magnetic Direction of Force in Vicinity of a Superconductor

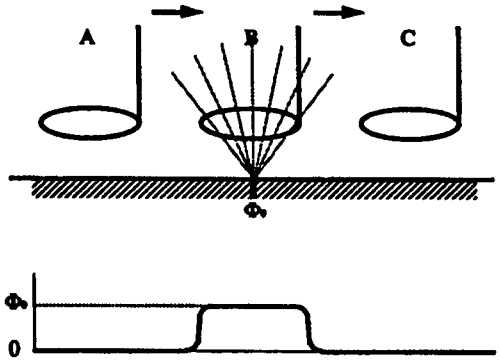


Figure 2. Change in Output of the Fluxmeter When the Detection Coil Passes Directly Above a Flux Quantum Trapped in a Superconductor

possible and will prevent the generation of a trapped flux by devising the shape and dimension of the ground plane. In this research, too, it is necessary to establish a means for detecting the presence or absence and the location of the trapped flux which appears in the unit of a flux quantum.

In the past, several methods have been developed for detecting a flux quantum trapped in a superconductor. However, these methods are either limited to the detection of a flux trapped in the electrode part of a Josephson junction or only possible for detection of a microscopic area, so that they are not suited for the present purpose. Accordingly, we developed a new technique. The features of this technique are 1) it is applicable to a plain superconductor other than the Josephson junctions, and 2) it is possible to carry out scanning and detection over a large area.

2. Summary of the Research

2.1 Principle of Trapped Flux Detection

The key point of our trapped flux detection method is to scan a superconductor in the vicinity of its surface by moving a detection coil in parallel to the surface. In accordance with this method, it is possible to reduce the influence of an external magnetic disturbance and to enhance the sensitivity to a trapped flux quantum. Namely, in the vicinity of the surface of the superconductor, the magnetic lines of force of an external magnetic field all become parallel to the surface because of the complete diamagnetism (Meissner effect) of the superconductor, and there do not exist magnetic field components that are perpendicular to the surface. Therefore, when the detection coil is placed parallel to the surface, the detection coil will never pick up the external magnetic field (Figure 1). On the other hand, the magnetic lines of force from the trapped flux quantum expand upward as shown in Figure 2, so that the

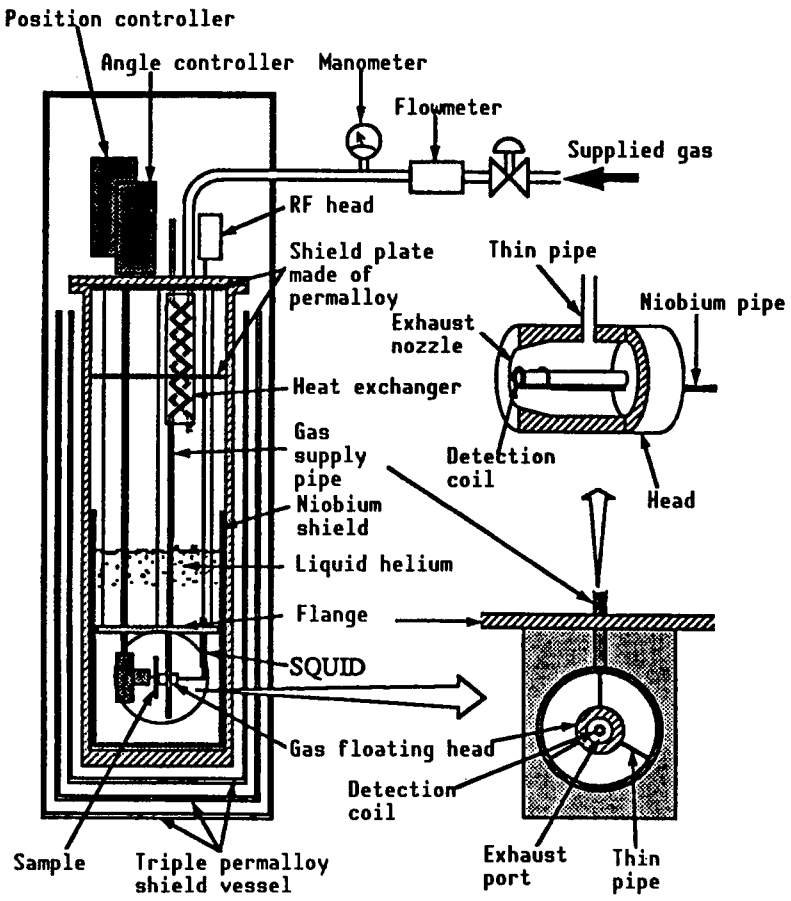


Figure 3. Schematic Diagram for Experimental Apparatus

quantity of flux that pass the detection coil—when the detection coil is scanned in parallel to the surface of the superconductor in the very close vicinity of the superconductor—becomes nearly equal to that of a flux quantum (Φ_0). By connecting this detection coil to the fluxmeter of a superconducting quantum interference device (SQUID) it is expected that the detection of the trapped flux can be accomplished with high signal to noise ratio (S/N). Therefore, we carried out an experimental study to demonstrate this possibility.

2.2 Gas Floating Method

The conditions required for the scanning of the detection coil include: 1) bringing the detection coil close to the surface of the superconductor to the extent possible; 2) keeping the height of the detection coil constant; 3) preventing the generation of vibration or mechanical damage due to contact between the detection coil and the superconductor; 4) suppressing magnetic noise; and 5) permitting operation in liquid nitrogen and in liquid helium. As a method that satisfies these requirements, we developed the gas floating method.

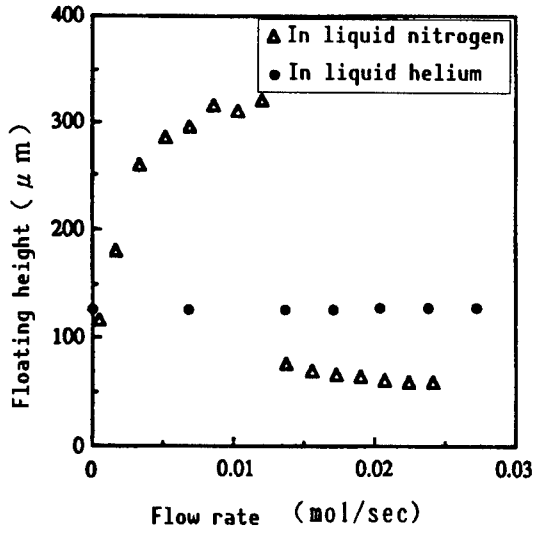


Figure 4. Relationship Between Flow Rate and Floating Height

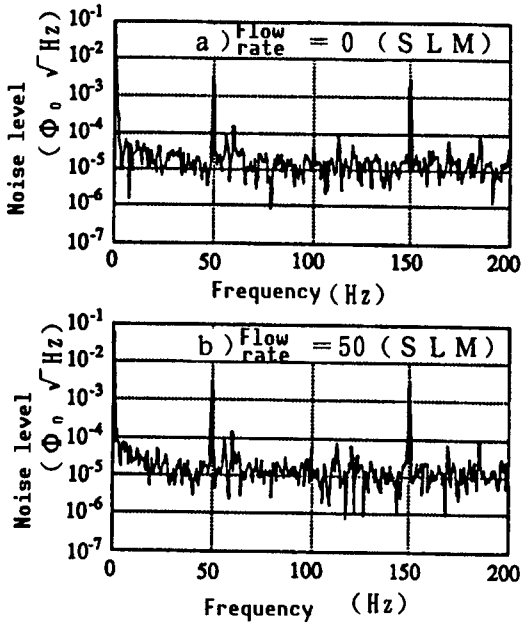


Figure 5. Comparison of Noise Levels With and Without Gas Supply

The experimental apparatus is as shown in Figure 3. The flow rate of helium gas is controlled by a controller in the room temperature section. Helium gas squirted from an exhaust port at the center of a head fitted with a detection coil (gas floating head) flows radially in the gap between the head and the superconductor. This gas flow exhibits an autonomous control mechanism which keeps the floating height of the head at a constant level. The relationship between the floating height and the flow rate is shown in Figure 4. In the experiment in liquid nitrogen, in the region where the flow rate is larger than 0.014 mol/sec (20 SLM), generation of a negative pressure becomes stronger with the increase in the flow rate according to Bernoulli's theorem, reducing the floating height of the head. On the other hand, in the experiment in liquid helium, a region of negative gradient is not observed so that there is room left for further examination. However, the variation of the height of the detection coil when it is scanned (actually, the superconductor sample is scanned) is about ±3 percent, and the increase of the noise level of the SQUID fluxmeter due to vibration caused by squirting helium gas into liquid helium is so small that it cannot be measured (Figure 5).

2.3 Detection of Flux Trapping

Using the measuring apparatus shown in Figure 3, magnetic field distribution on a superconductor sample was measured. The sample is a 2-inch wafer whose one-half portion is covered with a sputtered niobium film. The result of sputtering is shown in Figure 6. A sharp peak that seems to be due to magnetic impurities appears in the one-half of the wafer where no niobium film is deposited. However, except for this peak, signals from the half plane with no niobium film are smooth compared with the signals from the half plane where

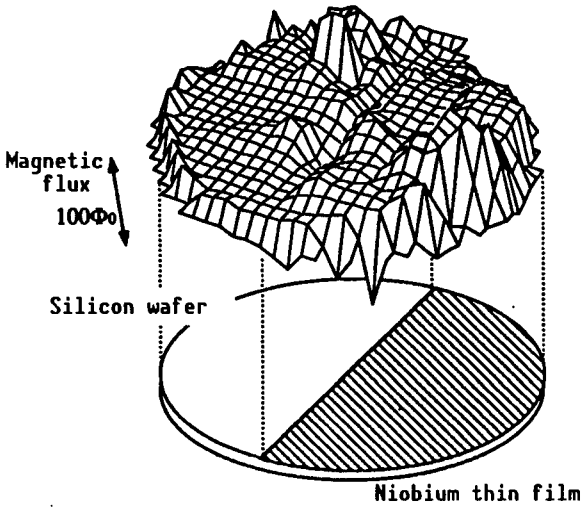


Figure 6. Two-Dimensional Magnetic Field Distribution Directly Above a Silicon Wafer Sample With a Niobium Thin Film Formed on One-Half of the Plane

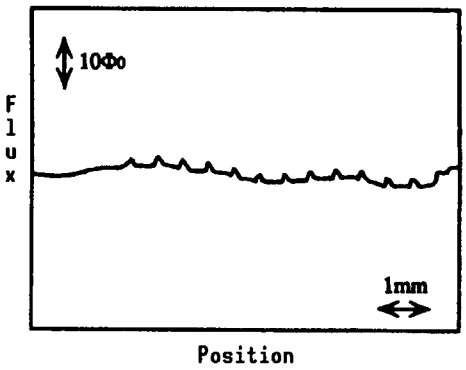


Figure 7. Output of SQUID Fluxmeter When the Detection Coil Passed Directly Above the Superconducting Striplines

the niobium film exists. This suggests that the flux trapped in the niobium film generates a roughness in the magnitude of the magnetic field on the surface. Further, the valleys that appear along the periphery of the niobium film shows that there exists a magnetic field which is stronger (downward) than that at the periphery due to the fluxes excluded by the complete conversion of the niobium film to the diamagnetic body (Meissner effect). In this case the gentle variation in the background was 65 Φ_0. Then, the material of the sample holding system was changed in succession from stainless steel to an aluminum alloy. Next, the detection coil was scanned over 12 striplines with 400 μm width. The output is shown in Figure 7. Due to the complete change to the diamagnetism of the striplines, the magnetic fluxes pass through the gaps between the striplines and outside of the striplines on both ends. Because of this, the magnetic field near the surface is modulated, producing 13 peaks (since the stripline direction and the scanning direction is not perpendicular with each other, the gap is greater than 400 μm). The amplitude of these peaks is about 2 Φ_0. On the other hand, the signal from a trapped flux quantum is close to Φ_0, as mentioned above. Therefore, the present result shows that our system has the capability of detecting a flux quantum trapped in a superconductor. The gentle variation of the background at this time was 45 Φ_0 in this example. However, when the material of the sample holder system was changed to aluminum alloy of titanium, the gentle background variation was reduced up to 2.4 Φ_0.

3. Future Development

The future research of the group will be directed along the following lines.

(1) To establish a technique for excluding a flux trapped in a superconductor by the use of a normally conducting hot spot.

(2) To obtain guidelines for preventing the flux trapping by acquiring knowledge on the correlation between the magnitude of the residual magnetic field and the shape and the dimension of the superconductor, and the generation of flux trapping.

In another important field of the technology of extremely low temperature generation, we clarified the behavior of the electroplated laminated bellows that was devised by us by the use of stress analysis due to the finite element method, and clarified experimentally the fatigue strength of the electroplated nickel film which is the bellows constituent material. Currently, we are engaged in the theoretical study aimed at a new system for gaseous expansion in the refrigerator.

Kimura Metamelt Project (1990-1995)
-Quest for Solution of Melt Materials-

Shigeyuki Kimura
Project leader

1. Summary of the Project

A melt plays a vital role as an important state which affects the quality of the product in the manufacturing process of a single crystal material or a glass. Although a melt has a certain structure since its interatomic interaction is not as small as in a gas, it has a fluidity greater than a solid, so that it is not easy to obtain knowledge concerning its fine structures. For that reason, despite its long history of research, the structure of a melt is understood so far in statistical form alone and only partially.

In recent years it has been known empirically that the properties of a melt varies with the lapse of time; namely, the properties of a melt reveal changes with time even when its surrounding conditions are kept constant. For example, it is known that there are differences in the quality of crystallized product for a just-diffused melt and for a melt which has been left standing for a certain length of time; that the coefficient of viscosity measured by lowering the temperature of the melt from high to low; and the time required for obtaining a constant value (the relaxation time) varies with the rate of drop of the melt temperature, etc. These phenomena are thought to be due to changes in the structure of the melt, but this is only conjecture.

The recent advancement in the technology that uses radiation or neutron beams is benefitting the research on the structure of the melts. Moreover, for materials which permit the utilization of light scattering, a method has been developed which analyzes wide area structures which might be called melt textures by the use of Rayleigh scattering. Furthermore, the environment for the study of melts is becoming arranged with groping for the combined use of direct viewing and computer simulation as a method of analyzing the behavior of high temperature melts.

Under the subject study, we intend to elucidate the structural changes of the melts and to find new methods of crystal growth by focusing our attention on the temporal changes of the properties of the melts. More specifically, using the melts of semiconductors and oxides as the principal objects of research, we will trace the infrastructures of melts and their temporal changes by using various kinds of advanced analytical technologies including radiation. In addition, we will pioneer quick and accurate measurement techniques of various kinds of properties such as viscosity, surface tension, density and heat conductivity, and will search for the causes of the property changes by carrying out factor analysis of the measured values.

Moreover, we will carry out research on the direct viewing technology of melt fluidity and will clarify the influence of the property variations based on the structure changes by making the direct viewing technology correspond to the analytical result due to computer simulations that are carried out simultaneously. Furthermore, by executing crystal growth based on the understanding on these melt states, we will attempt to change the growth processes to correspond to crystal defects.

This research will not only contribute to the physical understanding of the fine structures and textures of the melts, which have not been clearly defined in the past, but it is expected to provide clues for the development of new materials and the creation of processing technologies in various advanced fields.

2. Principal Research Activities of Various Groups

This research will be focused on the overall problems of the melts by: 1) Tracing the fine structures and their temporal changes centered around the research of the melts that use radiation; 2) understanding property changes by means of quick measurement of melt properties; and 3) analysis of the melt flow through the correspondence between the actual measurement and the computer simulation. For this purpose, research will be advanced by gathering qualified personnel in diversified fields of crystallography, study of metals, mineralogy, physical chemistry, spectroscopy, electronic engineering, materials science, polymer chemistry, etc.

(1) Structure Training Group

The factors that cause property variations are probed by examining the fine structures of the melts by the radial distribution analysis (by X-rays and neutron beams), extended X-ray absorption fine structure (EXAFS), and small angle scattering (by X-rays and neutron beams). Moreover, the structural changes in the region between macro and micro will be traced by means of the Rayleigh scattering method that uses laser beams. Furthermore, the correspondence between these results and the results of computer simulations based on the structural models will be examined.

(2) Property Variations Group

Research will attempt to establish technologies for the precise measurement of properties such as viscosity, surface tension, density, and heat conductivity of the melts by means of the improved Stokes method, vibration damping method, laser Doppler method, etc., and to analyze the factors by investigating their heat history and retention time dependence. Moreover, a method will be established to compute the property variations of unknown melts by accumulating data on several representative chemical compositions and carrying out classification of the property variations. Furthermore, crystals will be produced from the melt states based on the classification of the variations and will measure the effects on the growth process and try to establish correspondence with the crystal defects.

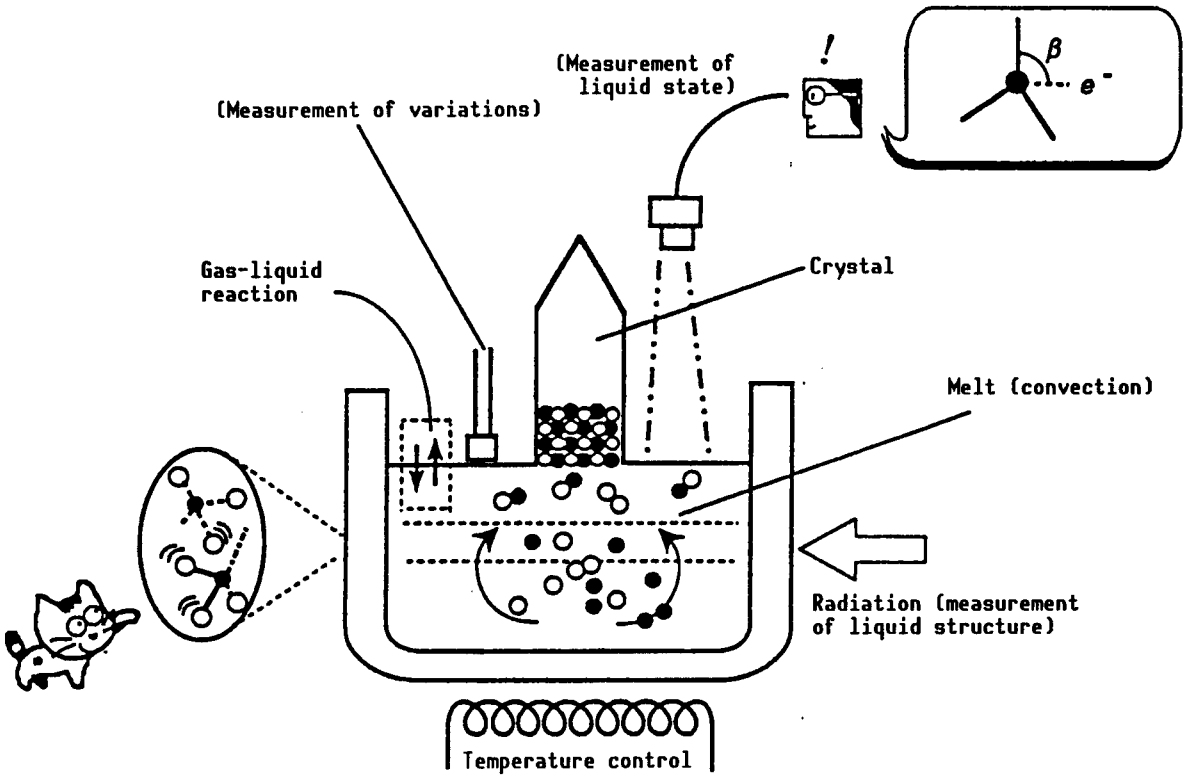


Figure. Conceptual Diagram for "Melt Movement"

(3) State Analysis Group

This group will attempt to establish a technology for visually analyzing the flow of the melt by carrying out development of a technique for direct viewing of the melt flow in the vessel and by carrying out fluid mechanical computations based on the properties and their variations of the melts. In addition, the application of the present technology to the understanding and control of the crystal growth phenomena such as Czochralski method and the unidirectional solidification method will be attempted.

3. Duration of Research

The research will be conducted from 1 October 1990 to 30 September 1995.

Yoshida Nanomechanism Project (1985-1995)
-The Way to Nanometer Technology-

Shoichiro Yoshida
Project Director

1. Introduction

In the present highly advanced information society which is about to enter the 21st century, a vast quantity of data processing medium is required to handle the symbolic object called information in a concrete manner. Hardware improves every few years in the degree of integration of the memory element. At present, the 1M bit memories are being mass produced and trial manufacture in the laboratory of the 64M bit memories is already being announced. Such progress is supported by the ceaseless effort to advance the manufacturing technology. The micron technology was advanced to the submicron technology, the submicron technology was advanced to the half-micron technology, and the technology for realizing the pattern width of 0.2~0.3 μm, called the sub-half-micron technology, is about to be achieved on the laboratory level. An extrapolation of this trend into the future will mean that it is necessary to have a technology for 0.1 μm; namely, the nanometer technology will be required at the beginning of the 21st century. For the realization of the pattern width of 100 nm there is required an element technology that has an accuracy on the order of 10 nm, and for the completion of the element technology of 10 nm there is required a technology which can realize a resolution on the order of 1 nm.

On the other hand, in the scientific field of biology, physics, etc., the objects of research are coming to deal with phenomena and behavior in an increasingly small region. In the field of semiconductors, research was started on quantum elements that deal with the phenomena that are characteristic of structures on the order of nanometers, and in the field of biology, too, effort is being put to the elucidation of molecular structures that correspond to the dimension of nanometers.

Now, let us consider the dimension 1 nm. As shown in Figure 1, 1 nm is the region which is adjacent to the world of atoms and molecules, and it is the region where materials begin to show characteristics that are noncontinuous. it is conjectured that a technology in such a region will be difficult to accomplish by a mere improvement of the conventional technologies. It is necessary to devise new methods by reexamining the conventional technologies from the level of atoms and molecules, and by adopting new ideas that take the behavior of atoms and molecules into consideration. On the basis of such ideas, the Yoshida Nanomechanism Project was started in 1985.

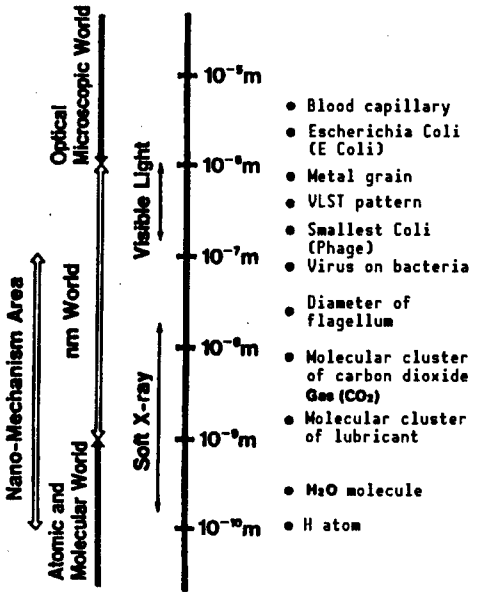


Figure 1. Nanometer World

2. Constitution of the Yoshida Nanomechanism Project

The research has been advanced by three groups. These groups are: the Fundamental Analysis Research Group, which carries out research centered around the elucidation of structures and characteristics through observation of the surface and the interior of objects on the order of nanometers; the Instrumentation and Control Research Group, which pursues the limits of the instrumentation and control technologies; and the Processing Research Group which conducts research on elimination and addition processing of the order of atoms. It should be mentioned that although the topics of research of the various groups are different from each other, research has been advanced under mutual influence based on the common ideas that deal with the behavior of atoms and molecules.

The topics of research were determined by mutual consent between the respective workers and the project leader at the time of initiation of the project. Each project is aimed at R&D of fundamental technological elements, utilizing the results obtained, but not aimed at development of the apparatus. Further, it is necessary to challenge research in new areas so that the selection of the topics anticipates some risk from the very beginning. For this reason, not all of the topics have been successful in obtaining the anticipated results.

The research topics of the various groups are as follows. The results of the main topics will be described in detail later.

(1) Fundamental Analysis Research Group

- Research related to scanning tunneling microscopy.

  · Development of a scanning electron microscope–scanning tunneling microscope (SEM–STM) hybrid device and observation of processed surface by STM.
  · Observation of biological samples.
  · Research on fundamental items toward industrial applications of STM.
  · Research on the twin probes STM as a new application of STM.

- Research on X-ray microscopy.

- Measurement of optical constants of materials for X-rays (joint research with the Processing Research Group).

(2) Instrumentation and Control Research Group

- Research on nanometer position control system.

- Research on nanometer length measurement system.

- Research on a fine motion mechanism that uses changes in the form of the traveling waves of PZT having a stroke of several millimeters and a resolution of subnanometers.

- Research on electrostatic linear motor micro mechanism by the processing of silicon using the semiconductor processing technology.

(3) Processing Research Group

- Research on the manufacture of a W/C system multilayered film by the high frequency sputtering method.

- Research on the manufacture of a W/V system multilayered film by the same method as in the above.

- Research on the manufacture of a W/C system multilayered film by the photo-assisted chemical vapor deposition (CVD) method.

- Research on the selection and the direct patterning of the SiO_2 system materials by the photo-assisted CVD method.

- Research on superflattening of the surface by low energy ion beam processing.

- Research on multilayered structures by intercalation as a reflection method in the X-ray region.

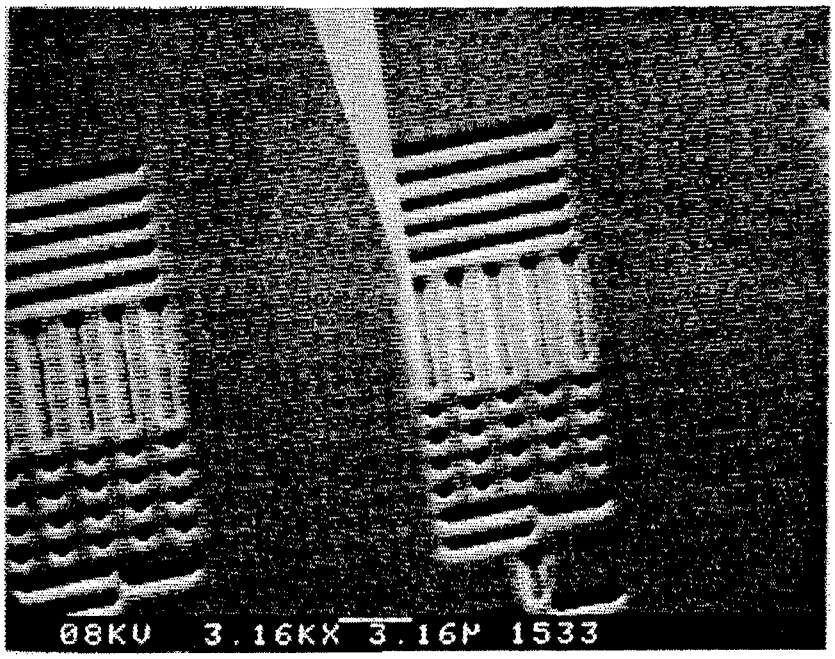


Figure 2. SEM Image of STM Tip and Sample
Sample line width is 0.9 μm.

3. Results of Research

(1) Research on Scanning Tunneling Microscopy (STM)

Since the fist manufacture by Binning, et al., of the STM [in the following, STM will mean scanning tunneling microscope or microscopy] technique has been advanced rapidly because it permits the observation of the three-dimensional images of atoms, and it is becoming an indispensable means of research in the field of surface physics. The scanning tunneling microscope is a microscope which utilizes a tunneling current that flows between the surface of a sample and the probe (tip) in which the change in the flow of the tunneling current with a change in distance is two to three orders of magnitude per single atom. This enables one to obtain a resolution the size of an atom. In addition, the STM technique has become capable of scanning and detecting the shape of a sample in the area of several micrometers with a perpendicular sensitivity of several nanometers thanks to the recent improvement in the scanning technique, etc. This makes it possible to measure fine shapes on the order of nanometers such as the measurement of the surface roughness of processed surfaces. Accordingly, research on the scanning tunneling microscope itself and research that utilizes STM are our very important research projects.

As a first step, we developed a hybrid device (SEM-STM) of an SEM and an STM for the purposes of observing processed surfaces or biological samples.[1] Since we adopted a system in which the STM mechanism is mounted on the sample stage within the SEM sample chamber, it became possible to switch the magnification over a wide range from the SEM magnification to the STM magnification. In particular, the image of a sample and a tip of the STM can be observed

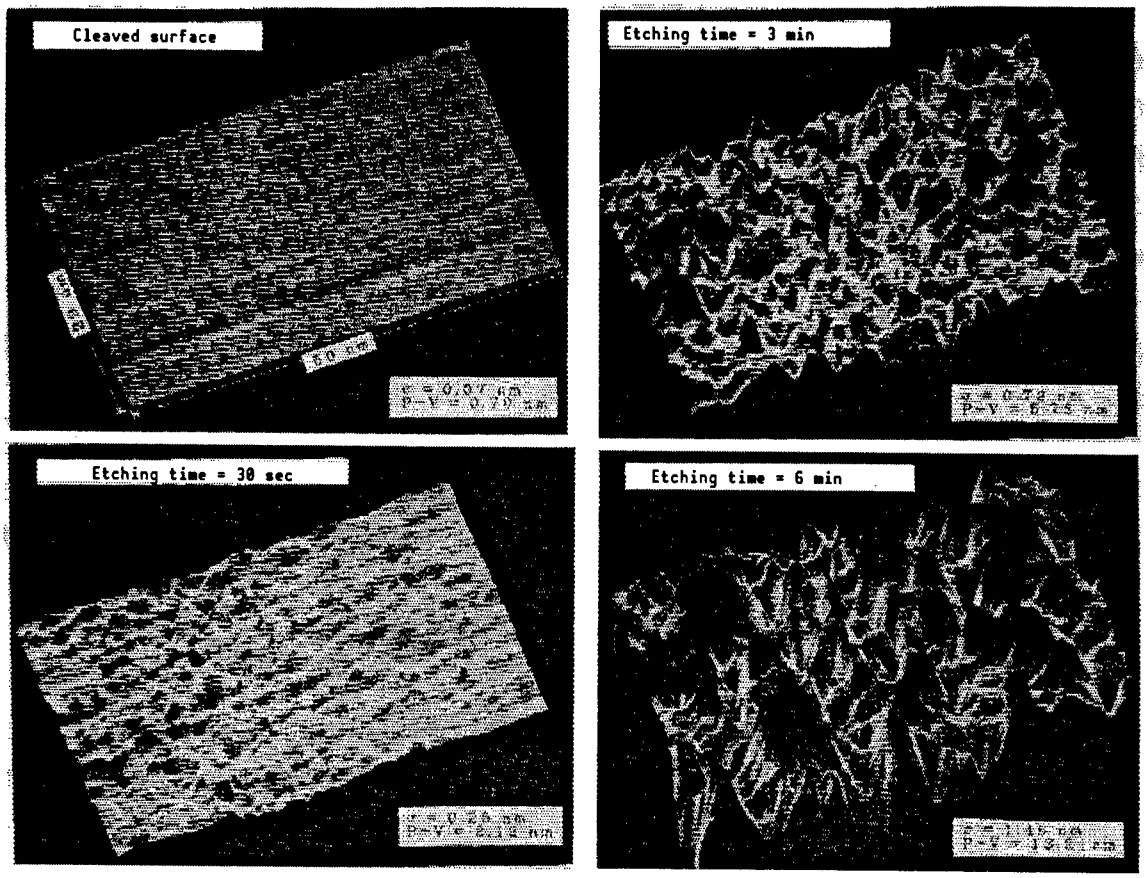


Figure 3. STM Image of Etched Kish-Graphite Surfaces

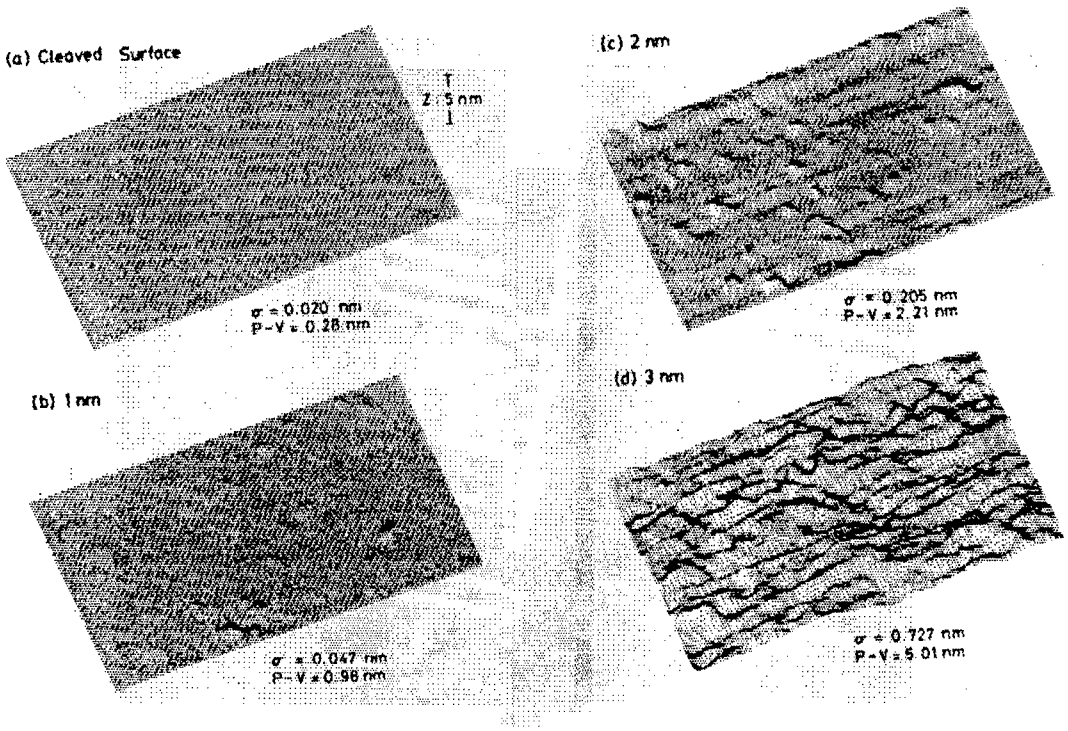


Figure 4. STM Images of Carbon Deposited Kish-Graphite Surfaces

simultaneously so it became possible to set a portion desired for observation using the STM to within an area of about 0.5 μm. In Figure 2 are shown the tip of STM and an SEM image of a sample. An STM image can be displayed as athree-dimensional and top view images on two CRT displays by changing over the switch. Using STM we observed as fundamental analysis of processing, the process of scraping of a graphite surface by the sputtering effect of ions, and the process of attaching of carbon atoms on graphite by the electron beam evaporation method were observed. In Figure 3 is shown the result of measurement of etching by the ion beam sputtering.

From the evaluation of the surface roughness it was found that the surface roughness is saturated at a value of 1 nm after about 6 minutes.[2,3] Further, the situation in which island structures are grown by evaporation are shown in Figure 4.[4]

The STM is becoming useful as a device for elucidation of biological structures on a molecular level. Biological samples, especially thick samples, lack electrical conductivity so that it becomes necessary to coat their surfaces with a conductive material. For the purpose of selecting appropriate coating materials, films with evaporated carbon were evaluated, and it was found that these films do not have high enough uniformity so as to permit one to obtain the images of the constituent molecules of living bodies, although images with sufficiently higher image than in the case of SEM can be obtained.

In fact, an observed image of flagellum showed a resolution higher than that of an SEM image, but it was not possible to observe the molecules. Note, however, that STM images are obtained for extremely thin samples of biological samples such as DNA. This image is considered to be obtained due to changes in the tunneling current depending upon the conditions of the sample when the tunneling current flows to the substrate through the sample, but its principle has not so far been clarified. As in the example, there are many unclarified areas in the tunneling phenomenon of biological samples, and in turn there exists a possibility of opening new areas by applying a pretreatment to the samples. As a result of study on the method of sample treatment by this project, we succeeded in identifying the molecular structure of flagellum by adding a dilute solution of glycerine, then lyophilizing the sample.[5] Figure 5 shows the result obtained. The significance of being able to confirm the structure analyzed by X-ray diffraction method, etc., directly as an SEM image is great.

The application of STM to industrial measurements is also being considered. Because of the high resolution, in particular the resolution in the horizontal direction, which is excellent by far in comparison to the conventional measurements that use a probe or light, application of STM as a surface roughness meter with high resolution is leading other efforts of application. In this case, however, there remain many elements that need be examined, such as the consideration for the increase in the irregularity of the work function caused by the measurement in the atmosphere, a scanning mechanism which can cover a wide area without distortion, the correction to be given in the measurement of a surface where materials with different work functions exist mixed even when the surface appears flat externally, the change in the tunneling current which originates from the shape of the tip, etc.

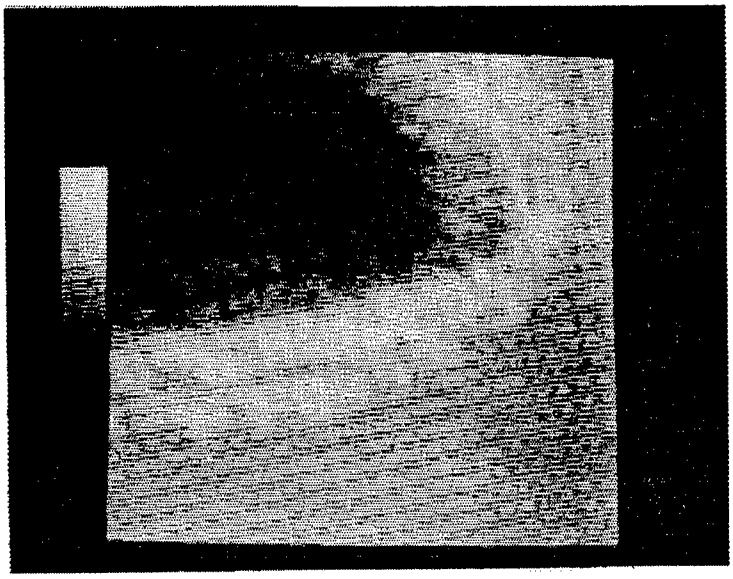


Figure 5. STM Images of Curved Flagellum Molecules Configuration Can Be Seen

Under the present project we discovered a system of obtaining a resolution on the order of atomic dimension, by employing a newly devised capacitor insertion method for the control of PZT which is an electrostrictive element used for the STM scanning to reduce the hysteresis and the creep of PZT, scan a wide area without distortion, and change over the switch.[6,7] The result of the experiment is shown in Figure 6.

Further, the shape of the tip matters in industrial applications because surface roughness far larger than atomic dimensions must be measured. The changes made in the STM image due to the shift in the point through which the tunneling current flows in relation with the position of the shape of the tip (having a roundness with radius of curvature of about 0.01 μm) and the surface roughness have been examined through various experiments and computer simulations. As a result, it became clear that the value of the surface roughness tends to be overestimated or underestimated depending upon the distribution of the ruggedness on the surface.[8]

As a new application of STM, we advanced a study on a twin probe STM which has a structure in which two probes are arranged extremely close to detect the tunneling phenomenon simultaneously. It is possible to detect the phenomenon of surface movement by a correlated processing of the signals from the two tips, or detect the surface condition of an extremely narrow region by using one of the tips for injection of current and using the other tip for detection. The first problem for this type of STM is the control for a parallel holding of the two tips parallel to the sample surface on the order of atomic dimension. In spite of this, we succeeded in obtaining an STM image of graphite atoms simultaneously in variable current mode by the use of two Pt tips. The result is shown in Figure 7.

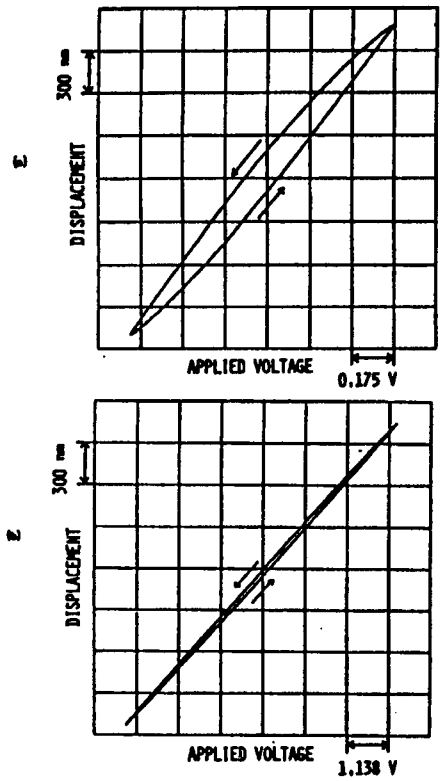


Figure 6. Improvement of PZT Hysteresis by Capacitor Insertion Method
(a) PZT (60 nF)
(b) 10 nF capacitor inserted

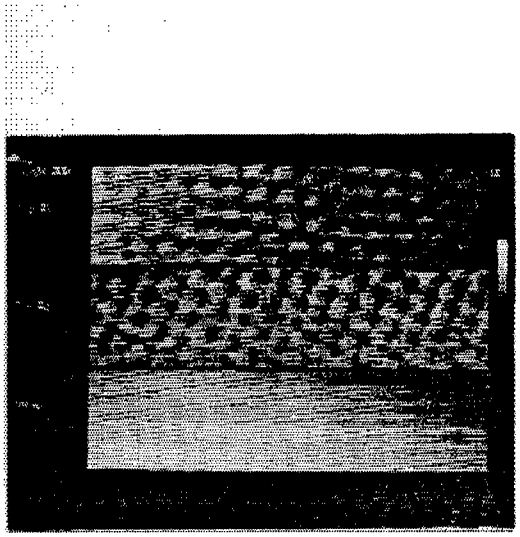


Figure 7. Graphite Image of Twin Probe STM
Upper: STM image of tip 1
Middle: STM image of tip 2
Lower: Height controlling signal

(2) Research on X-Ray Microscopy

The resolution of an optical microscope is limited by the wavelength of light used. In order to enhance the resolution it is only required to reduce the wavelength of the light to be used, and light in the soft X-ray region of 1~4 nm permits it to obtain images with high contrast because such light is absorbed selectively by the molecules that constitute a living body. For that reason, use as an X-ray microscope for biological samples is being studied. However, processing the elements for focusing X-ray images becomes difficult as the wavelength becomes small, and as to the materials to be used, it becomes necessary to examine the interaction with X-rays, such as absorption, from the fundamental aspect as to the decision for their use. Usually, a Walter type reflection mirror and a zone plate are used for the method, but the present project has been engaged in research on the phase type zone plate with a high-efficiency focusing characteristic to bring about an improvement by introducing a new idea.[9] As a result, we confirmed that it is possible to obtain a focusing efficiency which is 1.6 times that of the conventional Fresnel type zone plate by the use of the phase type zone plate.[10]

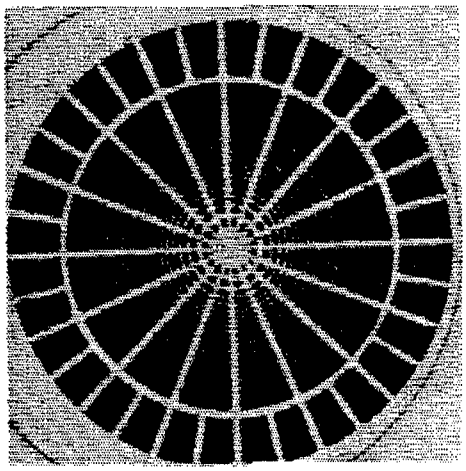


Figure 8. Zone Plate (Outer diameter is 0.2 mm)

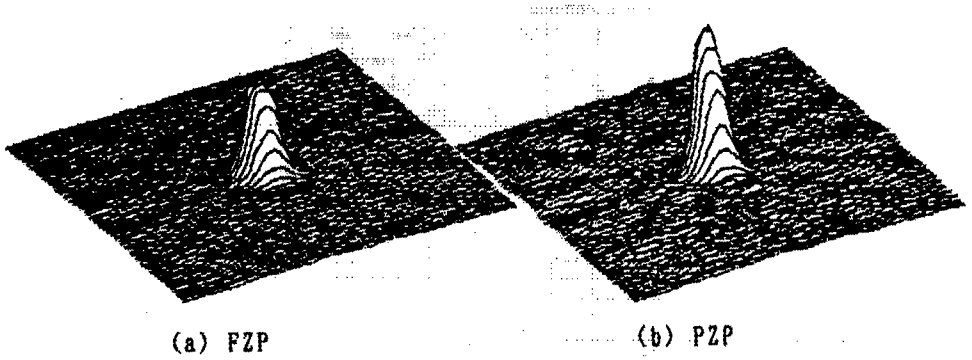


Figure 9. Focused X-Ray

Figure 8 shows a photograph of the zone plate, and Figure 9 the result of the focusing. In addition, a graded refractive index type zone plate was invented anew, and it was proved by computation that a focusing efficiency which is four times as large that of the Fresnel type zone plate can be obtained.[11]

(3) Measurement of Optical Constants of Materials for X-Rays

For the design of optical elements for X-rays it is necessary to know correctly the optical constants of the materials to be used. Although the optical constants of many materials have already been obtained by Henke, et al., these are values for bulky materials and they are imperfect as the values for thin films or for specific wavelengths such as at the absorption edges. For this reason, optical constants were measured for the design of X-ray multilayered films, soft X-ray zone plate, etc., which are the research objects of the present project. The measurements were taken of the reflection

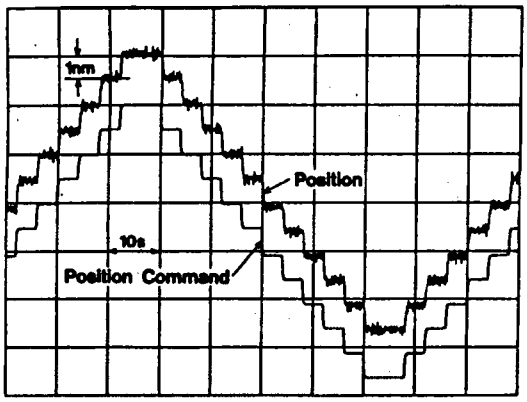


Figure 10. 1 nm Step Response

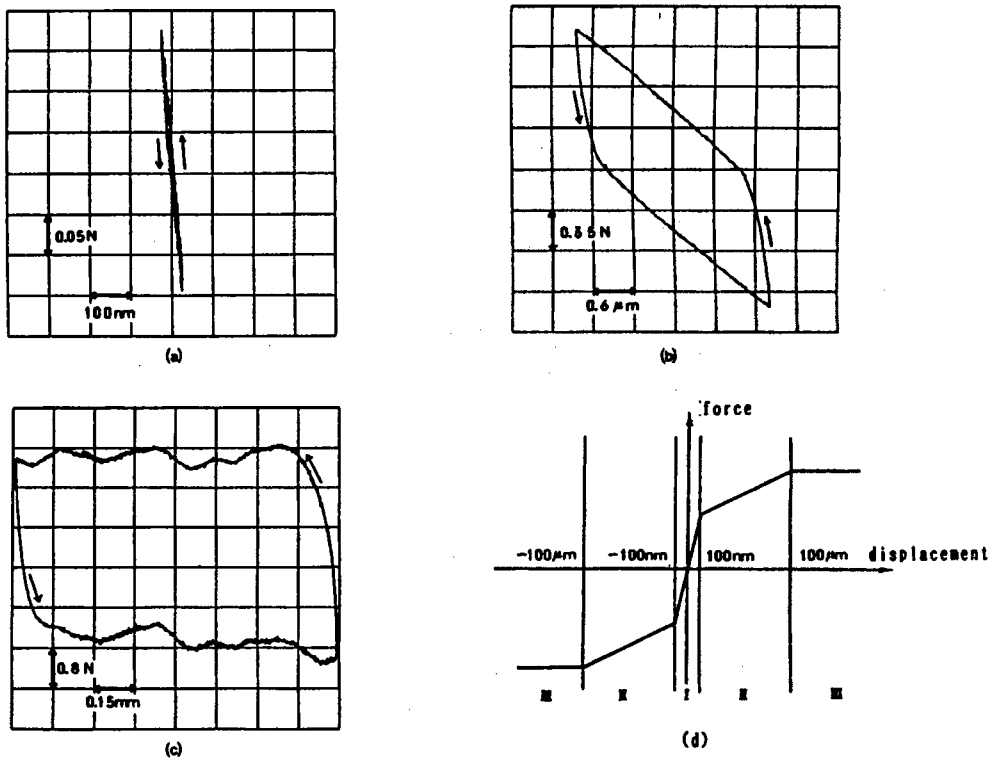


Figure 11. Balls' Behavior in Three Typical Regions
(a): nm region
(b): μm region
(c): several 10 μm region
(d): three typical region

and absorption characteristics for X-rays by using the SOR facilities of the High Energy Physics Laboratory at Tsukube. The optical constants are determined by fitting the data for the reflection and absorption characteristics to an equation representing the reflection from various layers which is based on the Fresnel equation and takes the scattering factor into account. In that case, it was made clear that the optical constants of the underlying material can be determined even by samples that have a thin oxide film attached to the sample surfaces.[12] In addition, from the absorption measurement there were obtained mass absorption coefficients for Al, Cr, Ni, etc.[13]

(4) Research on Nanometer Position Control System

The long stroke positioning technology has so far been considered that it is remote from the nanometer technology, but present project succeeded in the development of a nanometer position control system that has a controllability better than 1 nm by using a newly developed AC synchronous linear motor and ball roller guides. From Figure 10, which shows the 1 nm step response, it can be seen that there can be obtained a controllability of better than 1 nm which has no backlash even at the time of reversal. This characteristic was realized by a linear motor with excellent force resolution and a structure that does not have contact points except for the ball roller guides, and it was made clear in this characteristic that the principal point exists in the singular characteristic in the nanometer region of the ball roller guides.[14] As shown in Figure 11, the characteristics of the ball roller guides can be divided into three characteristic regions including the nanometer region. In the nanometer region the balls show the spring characteristic, and it was found that this characteristic is effectively used for the nanometer positioning. Generally speaking, this is precision position control that is studied by the use of two systems for coarse adjustment and fine adjustment, but the significance of the discovery of a characteristic that has so far been concealed as a result of turning-around of the point of view is very high.

(5) Research on Nanometer Length Measuring System

The length measuring system that uses an He-Ne laser interferometer has been used widely as a precision length measuring system, and a system that has a resolution on the order of nanometer is realized. However, a laser interferometer tends to be increasingly subjected to the ambient conditions, especially air fluctuations, as the resolution is made higher, generating errors in the measured values. In this project we devised a system which can eliminate the influence of the air fluctuations in real time by the use of laser beams with two wavelengths, and demonstrated its feasibility.[15] This system makes a correction by measuring the difference in the influences of the index of refraction of the air for two wavelengths by taking into account the fact that the influence of the fluctuations in the air is caused by density of the air resulting in changes in the index of refraction of the air; the index of refraction of the air for the ultraviolet region is different from that of the visible region. This principle utilizes the singular points (absorption edges) in the interaction of the air molecules and the laser beams (electromagnetic waves). Figure 12 shows the dependence of the index of refraction of the air on the wavelength.

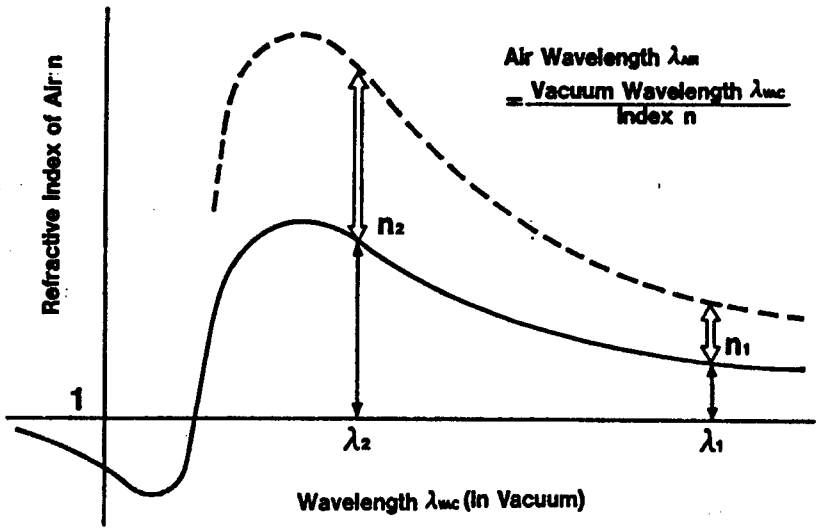


Figure 12. Two-Wavelength Measurement Theory

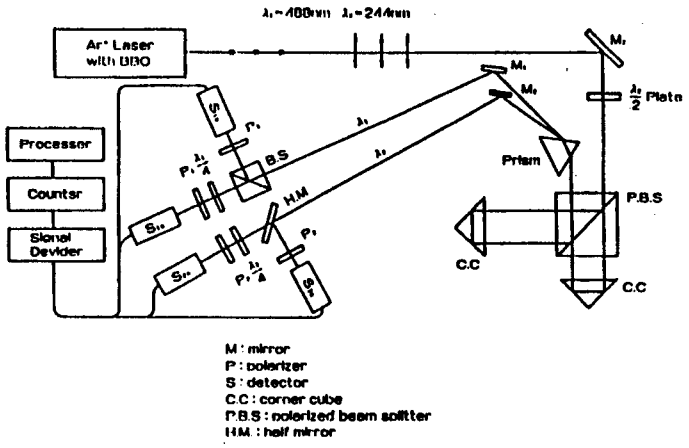


Figure 13. Schematic Diagram of a Two-Wavelength Displacement-Measuring Interferometer

An Ar laser beam with wavelength 488 nm and a laser beam with wavelength 244 nm obtained by converting the Ar laser by a second harmonic generator (SHG) material (BBO:β-BaB_2O_4) which uses a nonlinear optical element are arranged to pass the same interferometer optical path. These beams are separated into the respective wavelengths immediately before a detector; the beams are then detected, obtaining corrected measured values by real-time processing. Figure 13 shows an optical path diagram of the two-wavelength interferometer units.

The corrected value D is given by $D = D_1 - (D_1 - D_2)A$, where D_1 and D_2 are the measured values for the respective wavelengths, and A is a constant determined by the indexes of refraction of the air for the two wavelengths. The experimental data is shown in Figure 14.

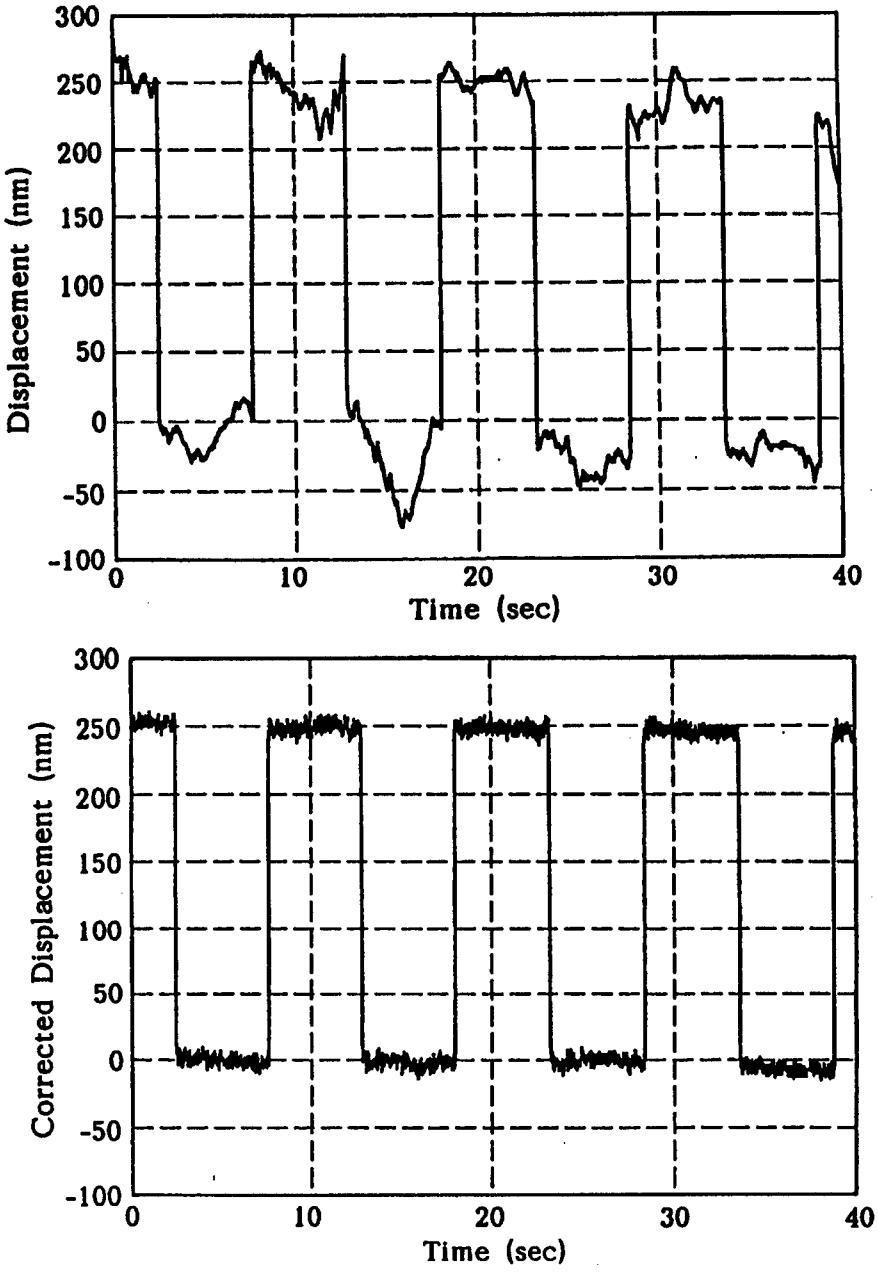


Figure 14. Elimination of Air Turbulence by Two-Wavelength Laser System Moving Mirror (c.c.) Is Being Moved 250 nm Back and Forth

(6) Research on Micro-Adjustment Mechanism

Although fine movements on the order of angstroms are being realized by the use of a piezoelectric element such as PZT, the limit of strokes of the element itself is 10 μm. The usefulness of an actuator having a resolution on the order of subnanometers and strokes of several millimeters is very high.

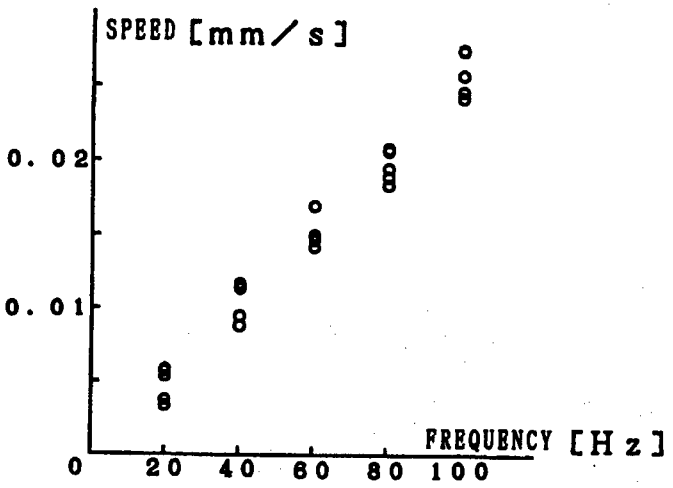


Figure 15. Characteristic of Ultrasonic Linear Motor Speed, Frequency

Under the present project a piezoelectric element array with periodic bimorph structure was forcibly driven by extending the principle of the ultrasonic motor to generate a traveling wave type deformation, and confirmed that it is possible to drive the piezoelectric device array over a velocity range which is broader than that of the conventional ultrasonic motor. The characteristic of the motor is shown in Figure 15.

(7) Research on Micro-Mechanism

In handling objects with a size on the order of micrometers, such as bacteria, there is required a micro driving element, so that a micro-mechanism of the dimension of several hundreds of micrometers has been studied. Under the

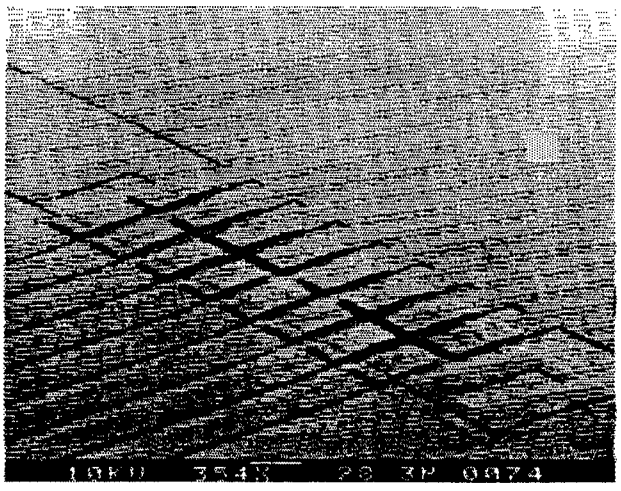


Figure 16. Fabricated Micro Linear Motor Test Model
Slide 1 L = 500 μm; W = 80 μm

present project we trial manufactured an electrostatically driven micro linear motor based on a new consideration. For the micro element the most important care is to be given to the friction. In the present system we employed a structure which makes both motions of shifting and floating by static electricity, and proved the effectiveness of the system by the use of an enlarged model. The linear motor under trial manufacture is shown in Figure 16.

(8) Research on Processing Method of X-Ray Multilayered Films

Because of the transmission through or the absorption by a matter, the number of X-rays reflected from the surface of the matter is only very small. For this reason, research is going on for X-ray multilayered films which reflect an effective amount of X-rays by combining a large number of small amount of reflected rays, in order to have reflected X-rays. However, the wave length of X-rays is of the order of nanometers so that the thickness of one layer of a multilayered film becomes several nanometers, and the roughness of the interface and the uniformity of each layer have to maintain an accuracy of subnanometers over several hundreds of layers. This is a processing of the order of atomic dimension, and it becomes necessary to make appropriate selections of the material to be used and to improve a processing method adapted to the material.

A multilayered film is constructed by a combination of a material with high density and a material with low density. A generally well-known combination is W/C. Further, in a specific wavelength region, it is known by computations that the reflectance of a matter increases in the vicinity of the absorption edge; the combination of Ni/V, etc., has proved to be effective. Based on these, we advanced research in the present project on the formation method of multilayered films for the W/C system, Ni/V system, and Ni/TiO_2 system that involves an oxide.[16,17]

As the processing method, we employed the magnetron high frequency sputtering deposition method which enables one to form at high speed a dense film with relatively large area. We tried to enhance the performance of the processing method by changing the device parameters and improving on the device. As a result, it was possible to obtain a maximum reflectance of 10.6 percent (for a wavelength of 54 Å and the angle of incidence of 64°) for a W/C multilayered film formed by using 100 layers with a pitch of 3 nm, and a maximum reflectance of 36 percent (for wavelength of 24.3 Å and the angle of incidence of 14.5°) for an Ni/V multilayered film formed by using 32 layers with a pitch of 4.8 nm. In addition, as a result of analyzing the properties of the manufactured films it was found that the density reaches only 60~70 percent of the bulky material which is considered to be the achievable limit by the sputtering method, so that it became clear that an entirely different method has to be employed in order to obtain still higher reflectance. Figure 17 shows a sectional photograph and Figure 18 shows reflectance of W/C and Ni/V multilayered films for the radiation in the soft X-ray region of SOR.

Further, processing by the photo-assisted CVD method is also going on simultaneously. The photo-assisted CVD method is a technique which was developed relatively recently, which enables one to form uniform films that

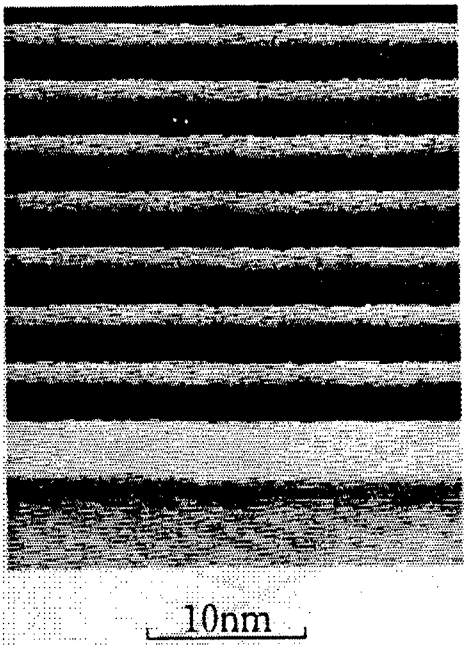
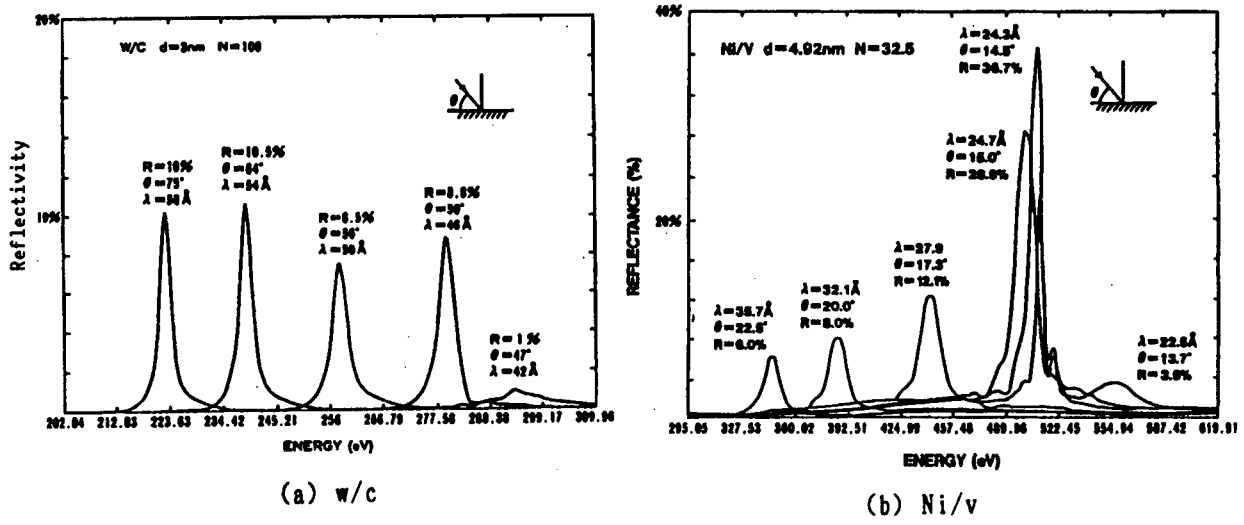


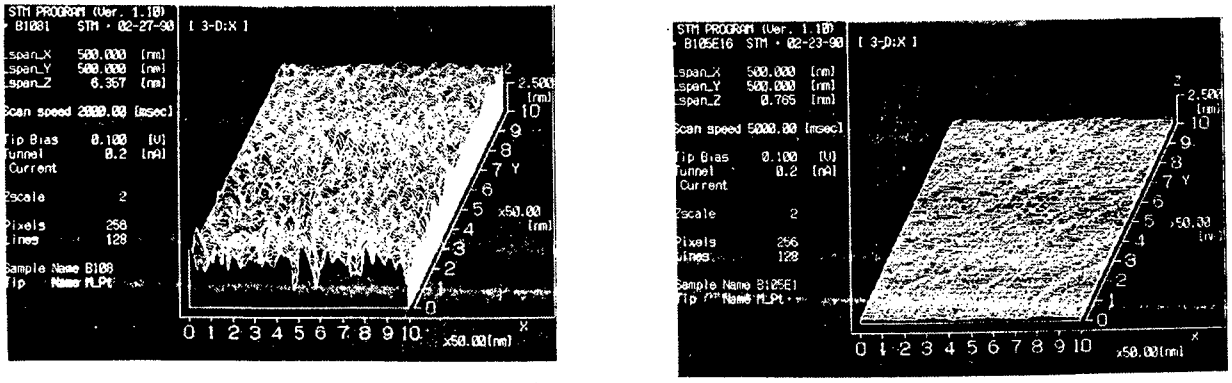
Figure 17. TEM Micrograph of W/C Multilayers (Part)
d = 3 nm; N =100
A substrate Si crystal lattice can be seen
at the bottom side.



(a) w/c (b) Ni/v

Figure 18. Reflectance of X-Ray Multilayers

have high controllability of density and high purity. We manufactured a multilayered film consisting of eight layers of W/C layer by the photo-assisted CVD method that uses ArF excimer laser, and obtained a reflectance of 40 percent for small angle reflection of a radiation having a wavelength of 0.15 nm.[18,19] In the future, research will be carried out on the technology for forming a multilayered film on the inner surface of a cylinder by making an



(a) Before process (δ = 0.4 mm) (b) After process (δ = 0.1 mm)

Figure 19. STM Images of W Film Surfaces

active use of the wide directivity of the deposition. In addition, the photo-assisted CVD method makes it possible to directly deposit fine patterns because it permits reaction only for the portions irradiated with light, and it has a new potentiality in conjunction with this field. In the course of this research we found a method for directly patterning an SiO_2 film on an Si substrate by the photo-assisted CVD method, and confirmed experimentally that it is possible to form an SiO_2 film only at portions on which the excimer laser beams are incident.

(9) Research on Super-Smoothing Processing With Particle Beams

The technologies for fine line processing and surface etching by means of particle beams such as ions and atoms have been known. However, the processing using such high energy beams roughen the surface. For this reason, in the present research we examined a method of forming super-smoothed surfaces with roughness on the order of atomic dimension by obliquely irradiating a sample with particles having low energies below 100 eV. Such a super-smoothed surface will be served as the substrate of a reflecting mirror and the processing by particle beams in a vacuum is an effective technology considering the addition of a multilayered film in the post-stage. As a first step of the research the processing with low energy Ar ions was carried out. As a result, we succeeded in sharply improving the surface roughness of a W film using ions of 50 eV, as shown in Figure 19.

4. Research Results and Future Prospect

The results obtained by the research under the present project are all basic items and are not those that can directly be tied to concrete devices or products, but on the contrary they seem to be applicable in the future to wider fields simply because they are fundamental. We believe that the research in this field will be actively used as an effective tool, not only in the industrial field that requires precision technology, such as semiconductor manufacturing, but also in the advancement of research in such fields of science as life sciences.

5. Conclusion

At the inception of the present project, the dynamic random access memories (DRAMs) that were being mass produced were those with 1 μm patterns. In addition, the term of the research in the general name of nanotechnology to which the research on nanomechanism belongs was not too well known even in silicon carbide circles. It is especially significant that a project which incentively studies a field of nanotechnology was initiated in such days.

As research progressed, the interests within and without the country were highlighted, and the demands especially from abroad for reports on the activities of this project have been increasing in number partly because Japanese research in this field is leading that in most other countries. In response to the request from the American Society for Precision Engineering, we have given reports on several occasions. A nanotechnology project, which is similar to our project, was started in the United Kingdom in 1986; a mission was sent to Japan in 1987, and a symposium sponsored jointly by Japan and the United Kingdom is to be held in the United Kingdom. In view of the worldwide exchange of ideas, we feel that it is recognized that the basic scientific technologies that will blossom 10 to 20 years from now are assets shared by the world.

In conclusion, we think that the progress of the research of the present project is due not only to the efforts of the workers but also to the members of the Research Promotion Committee and to those people who provided us with timely and appropriate advice in the course of the research. We would like to extend our deepest gratitude to all those who were involved in this project. We sincerely hope that research in this field will flourish in the future, producing many results and leading to the exchange of ideas in many fields.

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Tonomura Electron Wavefront Project
-Micro World Viewed With Electron Waves-

Akira Tonomura
Project Leader

1. Project

New observation means can become keys to the progress of science and technology. For example, on each occasion in the expansion of the observation region by the use of light, infrared rays, X-rays, γ-rays, etc., elucidation of the structures of matter, element compositions, bonding conditions of molecules, functions of biological matters, etc., have become possible by utilizing the properties of these radiations from various viewpoints.

In the field of optics, the appearance of laser beams brought about qualitative changes in the progress of instrumentation technologies. This may be said due to the fact that it becomes possible to fully utilize the intrinsic property as a wave of light. On the other hand, electron beams have been occupying important position as the means of instrumentation and analysis, but the information brought by them have mainly been those obtainable from the changes in intensities or energies. Due to the technological advances in recent years the situation has seen a drastic change through the discovery of a field emission type electron gun, which has excellent brightness and monochromaticity which made it possible to generate electron waves with high coherency.

Since the wavelengths of electron waves are one-thousandth to one one-hundred-thousandth of those of light, there exists a possibility of creating an excellent method for measuring and observing the three-dimensional structures of matters, distribution of electromagnetic field, etc., on the scale of atoms and molecules, provided that it is possible to utilize the phase information as in the case of light.

The theme of the present project is to try to see the pictures of matters and fields in relation to electron waves so that it will explore the method of actively utilizing information contained in the phase of electron waves. More specifically, it plans to devise new measurement and observation techniques by examining the fundamental interference characteristic of the electron wave. In addition, it will seek a method of displaying the phase change of an electron wave with accuracy approaching one one-hundredth of the wavelength by applying the image processing technique to the electron beam holography technology, and will challenge a measurement and observation technique that explores the world of quanta. Moreover, the hyperfine structures of matters and the electromagnetic field distribution in submicrometer regions will be observed by the use of the high accuracy phase measurement technique. Furthermore, research will be carried out on a method for reproducing the three-dimensional images of

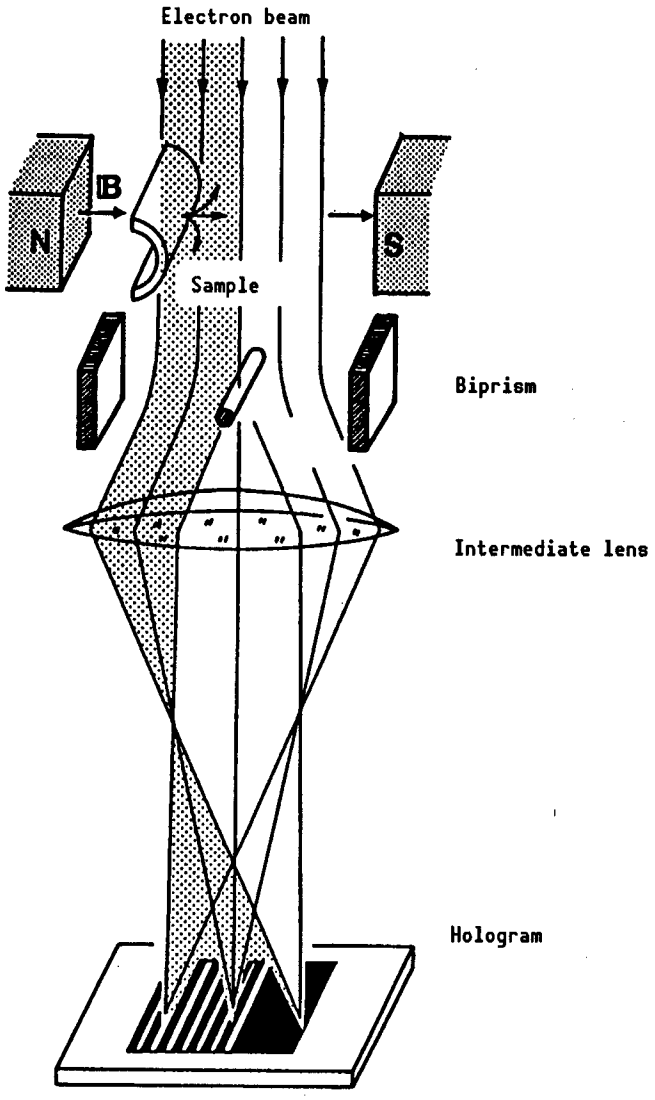

Figure 1. Conceptual Diagram for Hologram Formation Process
A schematic diagram for the process of observing the transmitted magnetic lines of force when a magnetic field is applied to a superconducting thin film.

matters and three-dimensional distributions of electromagnetic fields by using holograms taken from various directions.

Such research is expected to contribute substantially not only to the elucidation of natural phenomena in hyperfine regions, but also to the progress of advanced technologies which control and utilize the fine structures.

2. Principal Research Activities of Various Research Groups

The present research will develop an integrated research from the three directions of 1) fundamental coherence characteristic of an electron wave and new

measurement techniques; 2) a high accuracy phase measurement technique which uses the digital image processing; and 3) applications of the phase measurement and observation method to physics and biology. To achieve that purpose, the research will be pursued by gathering qualified personnel from the diversified fields of physics, optics, biophysics, and information engineering.

2.1 Fundamental Characteristic Group (Junji Endo, group leader; Hitachi Fundamental Research Laboratory, the place of work)

This research will examine the fundamental coherence characteristics of the electron wave, and will carry out at the same time theoretical examinations and experiments on the material information obtainable from the phase. In addition, it will carry out research on a measurement and observation method which utilizes the phase information, and will explore new knowledge which utilizes the measured result.

(1) The material information carried by the phase of an electron wave will be examined theoretically and demonstrated through the interaction between the electron wave and a matter.

(2) The measuring method of the fundamental coherence characteristics of the electron wave will be examined. In particular, the high-speed electron counting technique will be examined, the experimental feasibility of the electron beam version of the Hanbury-Brown-Twiss experiment will be probed, and the higher order coherence characteristics will be studied.

(3) The high-speed and high-accuracy hologram reproducing technique will be studied with the cooperation of the Image Analysis Group.

2.2 Image Analysis Group (Kazuo Ishizuka, group leader; Faculty of Engineering, Toyo University, the place of work)

This group will carry out research on the method for reading the phase distribution at high accuracy from an interference pattern by means of a digital image analysis method that utilizes computers.

(1) A digital image processing system, which will fully read in detail and interpret matter information recorded in an electron beam hologram, will be pursued.

(2) An algorithm which will determine the three-dimensional shape of a matter or three-dimensional distribution of electromagnetic field from a plurality of holograms taken for different directions of incidence, will be examined.

(3) An algorithm which will correct for the spherical aberration of the objective lens which restricts the resolution of the electron microscope will be explored.

(4) A real-time hologram reproducing image processing system will be developed under joint research with the Fundamental Characteristic Group.

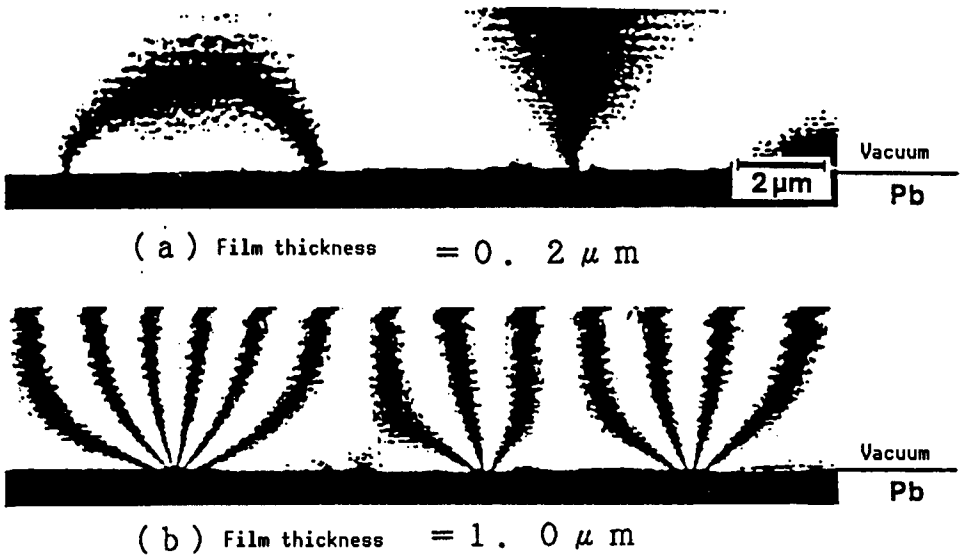

Figure 2. Observation of Superconducting Flux Quantum
The figure shows the situation where the magnetic lines of force that penetrate a Pb thin film from bundles in the unit of the flux quantum. A thin Pb film changes its state from a first kind superconductor to a second kind superconductor when the film thickness is reduced. It can be seen that a characteristic difference appears in the distribution of the flux quanta.

2.3 Measurement and Observation Group ((Takayoshi Nishi), group leader; Hitachi Fundamental Research Laboratory, the place of work)

This group will pursue the possibility of establishing a new ultimate measurement and observation method by applying the high-accuracy phase measurement method studied by the above-mentioned group to physics and biology.

(1) To explore the possibility of observing biological matters by the phase difference contrast method.

(2) To achieve image observation on the atomic level by improving the resolution through correction of aberration of the electron lens.

(3) To analyze three-dimensional structure of matters and fields under joint research with the Image Analysis Group.

3. Research Execution System

During FY 1989 an electron beam holography apparatus was introduced, and research on the basic interference characteristics is being studied under the joint research of the Fundamental Characteristic Group and the Measurement and Observation Group. Further, a hot cathode type electron microscope was introduced, and facilities for manufacturing various kinds of thin films for high resolution electron microscope observation are being arranged.

At present, a high definition hologram reproducing image processing apparatus has been introduced, and we think that the research has entered the stage of full-scale operation.

4. Duration of Research

The research will be conducted from 1 October 1989 to 30 September 1994.

VOLUME 3

Molecular Dynamic Assembly Project
-Flexible Functions of Bimolecular Machines-

Hirokazu Hotani
Project Director

1. Overview

Biological organisms effectively perform highly sophisticated functions such as self-organization, self-replication, energy conversion, information propagation and processing, and selective transport of substances. The unit elements which perform these intricate functions are thought to be assemblies of such biological molecules as proteins and lipids.

In the past, the dynamics of molecular assemblies were considered to be deterministic like those of man-made machines, which have unique output responses to given inputs. But as research on molecular assemblies has progressed, various phenomena which cannot be explained by this analogy have been discovered. Molecular assemblies have been found to be capable of changing their own energy conversion and information transmission functions in response to environmental changes. Such assemblies are termed "supramolecules."

For example, the flagellar motor, which powers bacterial flagellum rotation, operates as a result of proton flow into the cell through the motor. The relationship between the angle of rotation and the number of protons flowing into the cell is not fixed, but varies according to environmental conditions. Specifically, when the load is reduced, the motor rotates with fewer protons than before; the motor is designed in such a way that it can rotate smoothly even if there are not enough protons flowing into it. Such an input-output relationship is called "loose-coupling" which can also be observed in the acto-myosin system in muscle and proton ATPase.

2. Research Strategy and Objectives

The goal of this project is to understand why supramolecules function properly in thermally fluctuating environments and to explore related engineering applications. This could lead to the creation of "intelligent" molecular systems which can change their morphologies and function in response to environmental changes.

Thus, one of the project groups (Fundamental Analysis) is analyzing the structures of the flagellar motor, acto-myosin system, and flagellar filaments by direct observation. Their microstructures are being analyzed by such means as X-ray diffraction. Three-dimensional views of supramolecular structures of the dynamics of supramolecules will be clarified by measuring their momenta and the amounts of such substances as ATP and protons entering and leaving them.

Also, methods for reconstituting supramolecules in vitro with such biological functions as environmental adjustability, self-assembly, self-repair, self-dissociation and memory, are being pursued by creating new three-dimensional structures by modifying the constituent proteins of supramolecules. Attempts will be made by utilizing self-assembly function of supramolecules to create microstructures whose sizes and shapes can be controlled freely and precisely. They will have information transmission and conformation transition functions, and their functions and characteristics can be controlled by varying thermal, light, and other inputs.

A search will be made for ways to utilize the characteristics of supramolecules for constructing biosensor and biochip systems capable of sensing, processing, and judging external information. Specifically, by utilizing methods of embedding proteins in membranes and of artificially modifying proteins, attempts will be made to endow single supramolecules with multiple functions.

Bacterial Flagellar Motor

Shinichi Aizawa
Higher Functions System Group

Bacteria such as *E. coli* and *Salmonella* can swim by rotating their flagella, which are helical filaments with a well-defined pitch and diameter. The torque for flagellar rotation is generated by the flagellar motor at the base of the flagellum. The energy source of this torque generation is not ATP (an energy-rich phosphate compound most commonly used in biological systems), but the flow of protons through the membrane. The elucidation of detailed mechanisms of the energy transduction in the flagellar motor is under way.

Measurements of the flagellar torque have been achieved by the analysis of swimming speed of cells, or by the measurements of spinning rate of tethered cells. In both cases, the intrinsic rotational rate of a single flagellar motor cannot be determined because of bundle formation of the flagella or because excessively high loads are imposed on the flagellar motor. We have developed a laser dark-field microscopy system whereby the rotation of the single flagella can be analyzed with high resolution in time and space, and have shown that the motor is able to rotate at the maximum speed of 250 Hz under our conditions. We also found that the motor is able to pause or reverse its rotational direction within 1 ms and that the fluctuation of rotational speed is less than 5 percent.

The structure of the flagellar motor has been described morphologically on the basis of electron microscopic observation. We have devised a method of purification of the motor in large quantity and have analyzed each component of the motor biochemically. The primary structures of most of the components have been determined. We have used genetic engineering techniques to amplify single components of the motor for structural studies, and have successfully identified the Sring, a structure of the motor which has defied identification for a long time, as part of the M ring.

Furusawa MorphoGene Project
-Searching for Genes Controlling Development-

Mitsuru Furusawa
Project Director

1. Overview

The phenomenon that a fertilized egg forms a complex and delicate organism through repeated divisions and differentiation into various types of cells is one of the most attractive themes in development biology.

"MorphoGene" is a general term for genes which control morphogenesis in the process of ontogeny. Transplantation experiments in amphibians and other species have demonstrated the importance of tissue interactions in morphogenesis. In lower organisms such as *Drosophila* and *Caenorhabditis elegans* (a nematode) genetic analysis of developmental mutants has been possible and links between certain genes and phenotypes have been found. Now molecular biologists have started to identify genes and proteins involved in cell-cell interactions and developmental processes.

Recently, a DNA sequence called a homeobox was identified in homeotic genes which determine the direction of differentiation of segments in *Drosophila* larvae. This homeobox DNA sequence is common to many animal species, including humans suggesting that developmental mechanisms may also be shared and that it may become possible to understand morphogenesis at the molecular level.

The main themes of this project are to search for the genes that control the fundamental processes of gastrulation and differentiation of germ cells (sperm and ova). To attain these goals, first of all, we have developed the following three new methods: 1) the "in-gel competitive reassociation method" for recognizing subtle differences in DNA structure in cell types from various stages of development. This was reported at last year's meeting; 2) the "equalized cDNA library" for making a complete catalog of mRNA from a given organism; and 3) the DNA amplification by the "lone-linker" method.

These methods should not only serve as powerful tools for developmental molecular biology but also contribute to progress in studies in agricultural and medical fields.

The project is being carried out by three groups: the Gene Search Group, the Gene Expression Group, and the Gene Control Group. The following briefing summarizes the current research activities of these groups:

(1) Gene Search Group

It is known that the eggs from a *Xenopus* female frog, named No. 65, stop developing just prior to gastrulation and lack a 38K protein which is present in wild-type eggs. We are searching for the protein and specific cDNA that codes for it from the wild-type. In addition, we are pursuing the cloning of mRNAs for dorso-ventral axis determining factors in *Xenopus*.

Concerning the study of germ cell differentiation, we are now making specific monoclonal antibodies against *Xenopus* germ plasm and we have already made antiprimordial germ cell antibodies. These antibodies will serve as markers for germ cell differentiation.

(2) Gene Expression Group

We are testing several alternative model systems to improve the sensitivity of techniques which identify differences in the mRNA or DNA between cells or tissues.

(3) Gene Control Group

This group's studies will provide insight into the regulatory mechanisms of gene expression. Moreover, several trials are in progress using the transgenic mouse system to attain site-directed integration of foreign DNA into mouse chromosomal DNA.

In the present meeting, we will report on the following three subjects:
1) cloning of cDNA for dorso-ventral axis determining factor(s); 2) the principle of making an "equalized cDNA library"; and 3) characteristics of antibodies against germ plasm and germ cells in *Xenopus*.

Dorso-Ventral Axis Formation in *Xenopus*

Chikako Yosida-Noro
Gene Search Group

In amphibians, gastrulation begins on the dorsal side of the embryo at a site opposite the sperm entry point. It is considered that sperm entry causes cytoplasmic rearrangements during the first cell cycle which result in the formation of the dorso-ventral axis of the embryo. However, molecular aspects of dorso-ventral axis formation in amphibians have not been studied so far.

On the other hand, in *Drosophila*, a fruit fly, analysis of mutants has revealed a group of genes that are involved in dorso-ventral axis formation. They form a cascade for serial activation of other genes. Some of them make products which show a gradient distribution along the dorso-ventral axis of the embryo. Among them it seems that the "key" gene is *dorsal*, which is a maternal gene causing activation of zygotic genes. Its transcripts distribute evenly in the embryo but the protein exists predominantly in ventral nuclei at the blastoderm stage and forms a decreasing gradient towards the dorsal side.

In order to clarify the molecular mechanisms of dorso-ventral axis formation in *Xenopus*, an African clawed toad, I decided to isolate *Xenopus* homologues of the dorsal gene. *Drosophila dorsal* is homologous to the proto-oncogene *c-rel* which exists in vertebrates. I used the polymerase chain reaction (PCR) to isolate a *Xenopus* homologue (XPB) of the proto-oncogene *c-rel* that corresponds to exons 4 and 5 of the human *c-rel*. This fragment hybridized to a 6.5 kb EcoRI fragment of *Xenopus* genomic DNA and detected transcripts in early embryos. As described for chicken *c-rel* transcripts, *Xenopus* also has three forms of transcript with sizes of 2.6 kb, 4 kb, and 7.5 kb.

Using this fragment as a probe, I screened a cDNA library from neural stage embryos and isolated ten positive clones out of 250,000 clones. I analyzed two of them: X-REL 3.0 and X-REL 1.7. X-REL 3.0 predominantly hybridizes to the 7.5 kb and 4 kb bands on Northern blots. These two bands are slightly detected from oocyte but go stronger from early gastrula and maximum expression is obtained from neurula to tail bud stages. On the other hand, X-REL 1.7 hybridizes to all three bands equally. The extent of expression of 2.6 kb band does not chang much throughout the early developmental stages. From the restriction map and by Southern blotting they are revealed to be independent clones.

By investigating the spatial distribution and the timing of expression of these genes at mRNA and protein levels, it should be possible to obtain some information about the molecular basis for dorso-ventral axis formation and approach the problem of what determines the starting point of gastrulation.

Germ Plasm and Germ Cell Differentiation in Xenopus

Masanao Watanabe
Gene Search Group

Multicellular organisms which reproduce sexually are composed of a great number of cells. These cells can be divided into two types. One is germ cells which have a role in handing down the life of the species to offspring. The other is somatic cells which form the rest of the body for maintenance of the individual body's life and ultimately leave no progeny.

One of the most fundamental questions in developmental biology is how germ cells and somatic cells differentiate from one cell (embryo). There is one hypothesis that germ cell determinants exist in the cytoplasm of the embryo and the blastmere containing it becomes germ cells.

In the early stage of frog embryo development, microscopically identifiable specific regions of cytoplasm near the vetal pole (the lower end of the embryo) has been reported. Although vetal cytoplasm is mostly occupied by yolk platelets, the regions devoid of yolk platelets exist like islands within vegetal cytoplasm.

The blastomeres containing such cytoplasmic regions will differentiate into primordial germ cells in the future. Therefore, this specific part of cytoplasm is believed to contain the "germ cell determinant" and so-called "germ plasm."

Electron microscope studies show that germ plasm is occupied with large numbers of mitochondria and that electron dense granular structures called "germinal granules" also exist among the mitochondria. These granules appear to contain ribonucleic acid (RNA) which may carry genetic information concerning the differentiation of germ cells.

However, there is little known about the molecular nature of germ plasm and germinal granules and their biological roles in germ cell differentiation.

With the aim of clarification of the roles of germ plasm (germinal granules) in differentiation of germ cells, we have attempted to isolate germ plasm and germinal granules from early embryos of frog, *Xenopus laevis*, and to identify protein components or nucleic acid (RNA) components of germinal granules. As a result, we were able to isolate germ plasm from 16-32 cell embryos and now we are producing monoclonal antibodies against germinal granules. Such monoclonal antibodies would lead to isolation of germinal granules and also identification of the nucleic acid (RNA) within it.

In addition, we have produced the monoclonal antibodies against the *Xenopus* primordial germ cell which recognized the surface molecules on primordial germ cells. Now we are identifying the nitrogen molecule and the epitope of the surface of primordial germ cell.

An Equalized cDNA Library

Minoru S.H. Ko
Gene Expression Group

The total number of genes in higher organisms is estimated to be under 100,000. However, constructing a cDNA library containing a full set of genes expressed throughout the life time of an organism, without redundancy, is a major challenge for modern biology. Toward this goal, I have tried to make a library of mouse fibroblastoid Ltk- cells with nearly equal representations of cDNa clones. Double-stranded cDNAs (ds-cDNAs) are synthesized from mRNA using an oligo(dT)-Not I primer. After shearing to 200~400 bp, a synthetic linear-primer, which has one blunt and one sticky end and an internal EcoR I site, is ligated to the cDNAs. The cDNAs are amplified by the polymerase chain reaction (PCR) using the ligated linker-primer sequence. After denaturation and reassociation of the ds-cDNAs, and isolation of single-stranded cDNAs (ss-cDNAs) by hydroxylapatite chromatography, the ss-cDNAs are again amplified by PCR. The cDNAs are digested with EcoR I and Not I, and inserted into a plasmic vector. Colony hybridization with eight probes of different abundance showed a reduction in "abundance variation" from at least 20,000-fold in the original library to 40-fold in the library constructed after three cycles of equalization. This indicates the usefulness of the current procedure for making equalized cDNA libraries.

Torii Nutrient-Stasis Project
-Eat Well, Be Well-

Kunio Torii
Project Director

Rats deprived of lysine, an essential amino acid, prefer to eat foods containing lysine. At the same time, their central nervous systems become more sensitive to lysine. Because of this, it is believed that animals are capable of seeking those foods which will help them maintain a normal nutritional balance. Whether a food is edible or not is determined by sight, smell, taste, and feeding experience. Altering the nutritional balance leads to changes in feeding behavior. The animal's cellular and neural metabolism also change to keep internal nutrients in balance. These complicated adjustments are called "nutrient-stasis."

Past research focused attention mainly on the effects of an excess or a lack of a vitamin, mineral, essential amino acid, or other nutrient, and with the effective utilization of such a specific nutrient. Few studies have dealt with the actual food choices of an animal. However, now it is possible to measure nerve activity and sample brain metabolites during feeding. This can be done long term on animals that are free to move about and are not drugged. This allows us to observe the physiological details of an animal's desires.

This project will seek the nutritropic mechanisms by which animals change their diet in response to changes both external and internal to the animal. The project will observe the feeding choices of animals given diets with varying nutrient balances and of animals at different life stages. The project will also observe the choices of animals suffering from diabetes, hypertension, renal failure, or other diseases or problems. The nitritropic mechanisms of undrugged and unrestrained animals will be followed by continuously monitoring body fluids and changes in levels of hormones and growth factors in the alimentary canals, blood vessels, and brain. Nervous system adjustment mechanisms will be elucidated by measuring central nervous system response to nutrition-related signals from the alimentary organs, and by measuring changes in organ metabolism in response to stimulating the central nervous system. Hormones and cell growth factors will also be applied directly to selected parts of the brain in order to follow changes in feeding behavior and metabolism.

This research should lead to a better understanding of how animals maintain themselves through diet and how to prevent metabolic failure which occurs with age.

Kunitake Molecular Architecture Project
-Novel Functions Through Self-Organization of Molecular Materials-

Toyoki Kunitake
Project Director

The structural organizations of industrial materials such as metals and polymers are crucial to their performance and functions. The sophisticated functions observed in the living system such as energy transduction and information transfer are also directly associated with its intricate molecular organizations. It has to be noted, however, that there is a great gap in the extent of sophistication between nonbiological and biological organizations.

Recent rapid progress in biological science has opened ways to artificially construct molecular architectures which can mimic those of living systems. The biomembrane is formed by self-organization of component molecules (lipids and proteins) that are derived from their unique steric structures. The preparation of synthetic bilayer membranes has been successfully achieved in Japan and other countries by using a large variety of novel organic compounds. These compounds are composed of hydrophilic head groups and hydrophobic hydrocarbon chains in an analogy to biolipid molecules. Their particular structural features play an essential role in self-assemblage to bilayer membranes. This new synthetic approach in molecular architecture provides an exciting possibility of producing artificial organization leading to a new field of chemical science.

In this project, the major emphasis is placed on the methodological development for self-organization of the above-mentioned types of organic molecules. The subsequent preparation of functionalized molecular architecture and elucidation of their physicochemical characteristics in the form of surface monolayers, LB films, aqueous bilayers, and cast films are being conducted. We aim at the construction of molecular organizations which would possess particular electronic, magnetic, and chemical functions. Improvements of these functions will be attained by means of chemical modifications of simple assemblage and formation of multiply-composed organizations.

These studies should provide clues for the development of novel industrial materials that are equipped with sophisticated functions analogous to those of the biological organization and yet are characterized by stability and processibility of synthetic materials.

The laboratories of this project are set up at the Kurume Research Park on Kyushu Island. The total staff is 26, as of 1 October 1990, including project director, administrative staff, researchers, and technicians. The whole research team is divided into three subgroups. The current activities of each group are described below.

1. Fundamental Design Group

A systematic study is being conducted on the structure and the property of self-assembling surface monolayers, which are capable of molecular recognition at the interface. A variety of the physicochemical techniques was combined to study the molecular recognition by monolayers of several series of hydrogen bonding amphiphiles. It was shown that physiologically important classes of compounds—sugars, amino acids, and nucleotides—were bound specifically and strongly.

Surface sources measurement provides the presence of the attractive force between the two hydrophobic surfaces at an unprecedented distance of 300 nm. Scanning tunneling microscopy showed that some of the amphiphiles were aligned regularly on graphite. These results would be useful for direct measurement of molecular interaction.

2. Functional Architecture Group

A major target of this group is the preparation of self-organizing materials with novel electronic and magnetic properties. Specific introduction of transition metal ions into monolayer was accomplished by attaching metal binding units to self-assembling compounds.

A series of newly synthesized oligo (phenylenevinylene) amphiphiles formed stable monolayers on water. Some of these wholly π-conjugated monolayers produced Z-type LB films which showed nonlinear optical property.

Ultrathin films of silicates and aluminosilicates were prepared by using cast multilayer films as molecular templates. The morphology of the highly porous silicate showed surprising variations depending on the composition and preparative conditions.

3. Composite Architecture Group

Regular multilayer films were obtainable from mixtures of aqueous bilayer and polar bifunctional monomer. Photoirradiation and washing of the cast films produced multilayered two-dimensional molecular networks. Ultrathin two-dimensional networks were also prepared by two-dimensional crosslinking of composite LB films. Newly designed fluorocarbon amphiphiles gave uniform, stable monolayers.

Direct, Nanometer-Scale Measurements of Surface Morphology and Surface Interactions

Kazue Kurihara
Fundamental Design Group

Instruments for direct, nanometer-scale observation of surfaces, a scanning tunneling microscope, and a surface forces apparatus, have been set up in our laboratory.

Scanning tunneling microscopy (STM) is employed to image crystal structures of azobenzenecarboxylic acid derivatives which are adsorbed on graphite. A head-to-head configuration is seen in the derivatives with hydrogen terminated alkyl chains, while the other derivatives with bromine terminated chains show a head-to-tail configuration. These high-melting compounds can be adsorbed onto graphite from the liquid crystalline phase and provide tightly structured, very thin films, which are suitable for STM at room temperature.

Surface forces measurements reveal very long-range attraction, extending to a separation distance of near 300 nm between hydrophobic monolayers of a polymerized ammonium surfactant. These surfaces show no apparent repulsion. The attractive force can be described in a form of $F(D) = -A \exp(-D/D_0)$. The decay length D_0 is virtually independent of salt (NaBr) concentration of 1~ mM. On the other hand, A decreases with increasing salt concentrations. Long-range attraction of 300 nm distance has never been demonstrated, and is difficult to interpret in terms of the conventional van der Waals forces.

Molecular Silicates and Related Materials

Kanji Sakata
Functional Architecture Group

Silicate related materials with molecularly defined organization were synthesized in matrixes of synthetic bilayer membranes. Polysiloxane films synthesized from alkoxysilanes have varied microstructures composed of molecular-sized units such as spherically pored, multilayered, fiber-like, etc.

An amino group containing polysiloxane films with multilayered microstructure were also synthesized by this method. They showed rapid uptake and high capacity for complexity with Cu^{2+} ion, when compared with the corresponding polysioloxane synthesized without using synthetic bilayer matrixes. Synthesis of silica alumina thin films from aqueous colloidal silica and sodium aluminate was successfully conducted by a similar procedure. This silica alumina film has a multilayered microstructure with a high surface area (ca. 400 m^2/g).

The present methodology will be generally applicable to preparation of novel inorganic materials such as molecularly defined ceramics.

Preparation of Highly Stabilized LB Films by Molecular Design and Two-Dimensional Crosslinking

Tetuo Ueno
Composite Architecture Group

A negatively-charged surface monolayer, derived from a copolymer of maleic acid and a long-chain vinyl ether formed a polyion complex at the air-water interface with protonated poly (allylamine) in the subphase. Imide crosslinks were readily formed at 150°C as LB films. These two-dimensionally crosslinked (either ionic or covalent) LB films (two and six layers) covered stably the surface of porous fluorocarbon films.

Novel fluorocarbon amphiphiles were developed whose LB films could cover porous polymer films without polymerization.

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Masuhara Microphotoconversion Project
-New Chemistry by Laser and Microfabrication-

Hiroshi Masuhara
Project Director

Chemical reactions, if looked at over short time periods, consist of several elementary processes in combination. Also, chemical reactions generally proceed in an inhomogeneous field. The fundamental understanding of chemical reactions will be accelerated by elucidating reaction steps in each minute reaction field. The construction of an efficient conversion system of molecules and materials will perform its function by suitably combining and controlling transient processes in spatially arranged micrometer-size reaction fields.

Laser provides monochromatic, intense, and short-pulsed light that can be focused to a very small spot. This has been used as a tool to clarify elementary processes such as excitation energy relaxation as well as both electron and proton transfer in the nanosecond and picosecond time regions. Also, chemical reaction mechanisms have been elucidated for isomerization, dissociation, cyclization, and oxidation-reduction reactions by means of time-resolved laser spectroscopy.

Laser light has also been an energy source for chemical reactions and materials processing. Furthermore, it is recognized that the laser offers potential means to arrange local environmental reaction conditions such as polarity, viscosity, pH, and reactant concentration. Molecular confirmation and sol-gel transition of polymers can also be controlled by light.

On the other hand, microlithography, laser ablation, and scanning tunneling microscopy have greatly advanced in recent years. It is now possible to prepare micrometer-size spots and to study their chemical function. Consequently, a conversion system where such minute reaction sites are arranged spatially will probably be constructed. Laser light with micrometer resolution should be utilized in order to energize, interrogate, and control chemical reactions in this system. Thus, we believe that new chemistry will be developed by combining laser and microfabrication in molecular and materials systems.

From this viewpoint we consider that micrometer-picosecond spectroscopy, reaction, and fabrication will be an indispensable basis for the studies on chemical reaction and materials conversion. At the present stage we are developing dynamic microspectroscopy and microchemical manipulation methods, preparing micrometer-size spots with chemical function, modifying polymer surface photochemically, and examining micrometer-size effects upon reaction. On the basis of these results, we explore a new molecular and materials conversion system where temporal and spatial arrangements of the minute

reaction sites are given. This will contribute to various kinds of technology related to lasers and materials in addition to chemistry.

The project consists of three groups dealing mainly with lasers, microfabrication techniques, and conversion system design. During these two years, 16 researchers, including three foreign scientists, have been working. They have submitted 18 papers to international meetings and 45 papers to domestic ones.

(1) Dynamic Microspectroscopy Group
(in Kyoto Research Park Co., Ltd., Kyoto)

A new class of spectroscopic system, elucidating picosecond chemical processes in micrometer-size reaction field, is being developed which will open a new way to control chemical reaction.

A confocal laser scanning fluorescence microscope is combined with a mode-locked laser system, which gives molecular and electronic information with micrometer and picosecond resolutions. Such temporal and spatial analysis of dynamic structure and chemical reaction can be realized by developing a new data processing technique. This has already been achieved by introducing a convolved autoregressive model. The details will be reviewed in the following paper.

Surface and interface problems also require an analytical method with high spatial and temporal resolutions. Under total internal reflection conditions fluorescence from the surface and interface layers with the thickness of less than submicrometer is now measured in the picosecond time region. Our variable-angle, time-resolved total internal reflection fluorescence spectroscopy system is shown in Figure 1 [not reproduced].

Fluorescence and its dynamics of pyrene doped in segmented polyurethaneurea films were studied by the total internal reflection fluorescence spectroscopy. The differences in the environmental polarity and aggregation of the dopant between the surface layer and the bulk were elucidated. Pyrene molecules in the surface layer are located in the vicinity of polar segments while those in the bulk are incorporated near the less polar segments, as shown in Figure 2 [not reproduced]. By analyzing the incident angle dependence of fluorescence data, dynamic structure and chemical reaction will be revealed as a function of the depth from the surface.

(2) Microchemical Function Group
(in Central Research Laboratories, Idemitsu Co., Ltd., Chiba)

Using fabrication techniques, micrometer-size spots with chemical functions are created on the surface of polymers, metals, semiconductors, and so forth. Microlithography, laser ablation, chemical vapor deposition, and scanning tunneling microscopy are used for this purpose. These facilities are set in a class 1000 clean room.

Simultaneous patterning and chemical modification of polymer surface has been performed by laser ablation. The reactivity and physical properties of polymer

surface are changed by high density excitation, inducing adsorption and/or incorporation of functional molecules from surrounding gaseous atmosphere or aqueous solution.

Photoinduced electron transfer reaction can be controlled by using polymer films where some chromophores are oriented. This trial has been made possible by introducing microelectrode prepared by microlithographic technique. The photophysical behavior of molecules on electrode, near electrode, and between electrodes is different and is being studied by fluorescence spectroscopy.

A scanning tunneling microscope is now used not only for observation of a material's surface but also for preparing minute spots with chemical function. The materials and systems for this purpose are being researched. Organic thin film formation by CVD method is also being tried for the same purpose.

(3) Microconversion System Group
(in Research Institute for Production Development, Kyoto)

Characteristics of dynamic structure and chemical reaction in micrometer-order fields are studied by comparing the results with those in centimeter-order bulk. New molecular systems for controlling chemical reactions are also being researched. On the basis of these trials, this group explores a new integrated conversion system in which reaction steps in micrometer-size spots are driven, interrogated, and controlled with laser light and which will be highly efficient and selective in molecular and materials conversion.

We prepared micrometer-order rod-shaped photoresponsive gels and compared their photoinduced volume expansion behavior with that of bulk gels. It is worth noting that the response time of the micrometer-size gel is ~10 seconds while that of the bulk gel is ~10 minutes, as shown in Figure 5 [not reproduced]. We consider this type of effect crucial and expect that this minute photoresponsive gel will be an important element for controlling chemical reactions in a micrometer-order field. The viscosity and polarity changed by this photo-expansion are also hopeful factors in controlling the reactions.

Some approaches have been conducted for planting photo-functional molecules onto the polymer surface by a photochemical method. The reaction scheme is shown in Figure 6 [not reproduced]. Compared with photoresist and surface graft polymerization methods, the chemical nature is clear so that further applications are quite easy. A micropattern formation by these photo-functional molecules is also attained, which will be an important technique for creating a micrometer-size reaction field.

In order to conduct chemical reactions in a micrometer-size reaction field, we have set up a laser trapping-spectroscopy-ablation system. This makes it possible to choose a single small particle, to fix it at a certain position, to induce photochemical reaction on its surface, and to fabricate it. The details of this laser manipulation are described and its importance for the exploratory studies on microphotoconversion is discussed in the following paper.

Development of Dynamic Microspectroscopy Systems

Keiji Sasaki
Dynamic Microspectroscopy Group

Dynamic microspectroscopy systems, giving picosecond fluorescence and transient ultraviolet–visible absorption in the micrometer-size volume, have been developed. This has been achieved by combining a CW mode locked Nd:YLF laser system with a confocal laser scanning microscope.

The first system is for fluorescence spectroscopic measurement based on time-correlated single photon counting. Its spatial and temporal resolutions are 0.3 μm and 2 ps, respectively, while the spectral resolution of 1 nm is attained. The use of a confocal microscope enables us to monitor fluorescence with the depth resolution of 0.5 μm as well.

The second system is for absorption spectroscopic measurement. Picosecond pump and probe beams are coaxially introduced to the microscope, giving three-dimensional space resolution. This has never been realized by any other absorption microscopes.

These systems provide enormous data as a function of time, three-dimensional position, and wavelength. In order to analyze rise and decay curves, we have proposed a new fast and accurate analyzing method using a convolved auto-regressive model. The computation time of this method is much shorter than that of the conventional nonlinear least-squares method.

We have applied the present spectroscopic techniques to various kinds of molecular systems such as microcapsules, polymer films, microparticles, and oil droplets. The results demonstrate a high potential of the dynamic microspectroscopy systems in elucidating photophysical and photochemical processes in inhomogeneous systems.

Laser Manipulation for Microphotoconversion

Hiroaki Misawa
Microconversion System Group

Laser trapping has made it possible to choose a fine particle in solution and to fix it at a certain position in a three-dimensional space. Indeed, it has been shown that a single particle such as polymer latex, glass bead, silica gel, bacteria, and virus can be optically trapped by the radiation forces. Much attention has been paid to the study of the physical understanding of laser trapping itself and to apply trapping to biological systems. We are introducing this technique into the studies on chemical reactions and developing it as a chemical manipulation method.

We have set up a system which enables us to study spectroscopic and dynamic properties of an individual single particle in solution, to modify it chemically and/or physically, and to ablate it. This is named a laser trapping-spectroscopy-ablation system which is comprised of CW and pulsed Nd:YAG lasers as well as an optical microscope.

We demonstrate three-dimensional laser trapping of various particles and determine the trapping power to be on the order of pico Newton. This power is proportional to radiation intensity of the laser and is a function of the particle diameter.

Excimer kinetics in a single, laser trapped liquid droplet was measured by means of picosecond single photon counting. An interesting dependence of the dynamics upon the size of the droplet was confirmed for the first time.

An efficient ablation of a single, laser trapped latex particle dispersed in water was induced by using high intensity laser irradiation. It was demonstrated also that a single microcapsule containing organic reagents was chosen, transferred to a certain position, and ablated by the present system. This means that a manipulation tool for controlling chemical reactions in the micrometer-size volume is being realized by the laser trapping technique.

Nagayama Protein Array Project
-A Technological Form Emergent From Biosystem-

Kuniaki Nagayama
Project Director

Living organisms are complex structures built up through evolution. Molecular biology has shown that these structures assemble by themselves. The design scheme in living organisms, that is, the genetic information, appears as base sequences in nucleic acids which are expressed as the sequences of amino acids in proteins. This information is necessary for the formation of these sophisticated systems. It provides the rules for protein–protein interactions, protein–substrate interactions, and protein–nucleic acid interactions. However, this genetic information does not directly determine the internal environment, such as temperature and pH, inside living organisms. Protein interactions are the primary entities responsible for these complex structures without any outside control.

Generally, biological substances have been recognized to be inadequate as materials because of their instability, uncontrollability, high prices, poor purity, and difficulty in handling. These negative aspects, however, are being gradually lifted by the success of protein engineering. Biological macromolecules can then cast off their biological skin and acquire a novel form of intelligent materials. Exploring a technology which implements the biological principle of making biological macromolecules and assembling them into devices might be very intriguing. The recent advent of protein environment seems to be providing the basic technique to realize such a new technology whereby parts are automatically assembled to give final forms through the mutual recognition (interaction) which manifests itself in the structural information. Proteins are starting materials in our engineering, and complex structures designed for a special purpose, such as supramolecules and microcrystals with intelligent functions, could be self–organized in an appropriate working field. In this process of materials production, autonomous microscopic and mesoscopic ordering or arranging of proteins according to the built–in blueprint is the important step.

Protein Array

The protein array is a kind of protein form assembled and developed two–dimensionally on the surface of a liquid or solid. It would be two–dimensional crystals of proteins or complex patterns made of several protein species. Many attempts were made to prepare a monolayer protein film on the surface of water for that purpose, but they were neither reproducible nor very successful in making good crystals.

Recently, we have made some innovation for the two–dimensional crystallization of protein. The two–dimensional surfaces of metal liquids were adopted as a

hopeful alternative to the surface of water for a working field. The success of two-dimensional crystallization stimulated us to take a further step, where not only protein structures are to be elucidated but also new materials made of proteins could be organized as a protein array. It will investigate how protein assemblies are made alone and how the two-dimensional order in the assemblies is determined. The protein-protein interactions and the surface structures necessary for assembly will be designed and the proteins actually made through protein engineering. Assemblies will be made on a two-dimensional support such as mercury and their structures analyzed. The concrete targets are two-dimensional crystals, two-dimensional lattices, and multilayer films made up of monomolecular layers. In addition, the project will explore methods for reading and writing from the outside information carried in the assemblies.

Nishizawa Terahertz Project
-Exploration for Terahertz Semiconductor Devices-

Junichi Nishizawa
Project Director

The purpose of this project is to research the semiconductor devices and circuits which operate in the terahertz (THz: 10^{12}Hz) region. Terahertz region is the intermediate band between the light wave and the radio frequency.

The semiconductor devices are used up to 100 GHz (10^{11}Hz) and optoelectronic semiconductor devices such as the semiconductor injection lasers are the key devices in the optical communication systems.

The terahertz semiconductor devices and their related circuits will expand the stable frequency region from submillimeter to infrared.

There are three subgroups in our project located in Sendai: Basic Analysis, Functional Device, and Circuit Configuration. In the Basic Analysis Group, the photostimulated molecular layer epitaxy are used to obtain the very thin epitaxial layer for the very high-speed transistor and diode. Several kinds of devices such as mesoscopic static induction transistor (SIT), tunnel diode, semiconductor Raman laser, etc., are developed now. The circuits which operate as the mixer, detector, harmonic generator, traveling wave type optical modulator, etc., are also investigated.

Here we report on our project in more detail.

Semiconductor Raman Laser for Optical Communication

Ken Suto

The light wave signal having a bandwidth over terahertz frequency is very attractive for future optical communications systems. However, there is an essential problem. The present direct demodulation method by the pin photodiode or APD cannot meet such a system because of their frequency limits which are only around several tens of gigahertz.

The optical heterodyne demodulation using the semiconductor Raman laser will solve this problem. The semiconductor Raman laser acts as a frequency selective light wave amplifier or oscillator pumped by a local light wave oscillator. Therefore, it can pick up a desired frequency component, ω_{s1}, from a very wideband modulated light signal which is equivalent to light waves with many frequencies, ω_{s1}, ω_{s2}, $\cdots$, ω_{si}, $\cdots$. In order to realize a practical demodulator, a low threshold semiconductor Raman laser which can be pumped by a laser diode should be developed. The laser diode can easily change the light frequency by only changing the diode current.

We already reported the heterostructure semiconductor Raman laser having a waveguide structure with a GaP core and an $Al_xGa_{1-x}P$ cladding. There is a potential to build a high intensity optical field in a narrow core region enough to cause the stimulated Raman effect by a low pump power. However, there is the problem of how to launch the pump light. In our earlier reports, a window was opened by lithographic technique at a part of the reflector film of the resonator, which impeded the formation of very narrow waveguides. This time, we introduced a new structure in which the wavelength selective reflection film is transparent to the pump light and highly reflective to the Stokes light. As a result low pump power operation has been easily achieved, and we have succeeded in the operation of Raman lasers pumped by a lower power CW YAG laser instead of a Q-switch YAG laser.

This structure has no fundamental limitation in making further narrower waveguides necessary to realize the pumping by a laser diode. Therefore, the demodulation of the terahertz-modulated light has become a practical target.

Terahertz-Band Circuits and Measurements

Koji Mizuno

Measurement technologies for the THz region are required in the fields of high density communication, plasma diagnostics, remote sensing, radio astronomy, and molecular spectroscopy. We are developing GaAs Schottky diode detector/mixers, quasi-optical multi-element imaging arrays, and oscillator arrays and frequency multipliers for measurements in those fields.

We have developed fabrication procedures of Pt/GaAs diodes for obtaining low conversion loss and low noise mixers at the THz region. Processes of reactive ion etching and surface treatment of GaAs wafer surfaces have been improved in order to reduce diode diameter, to reach higher cutoff frequency, and to obtain low noise characteristics, respectively. The 0.8 μm diameter diodes have been successfully fabricated to have 11,600 K of the mixer noise temperature and 19.1 dB of the conversion loss at the signal frequency of 1.4 THz. These characteristics were measured by the hot/cold load method using room temperature and liquid nitrogen temperature eccosorbs as the loads.

A new approach for the development of region devices is offered by multi-element quasi-optical arrays, where many elements are arranged on a substrate whose dimension is larger than the operating wavelength. When the elements are antenna/detectors on a substrate, the device becomes an imaging array. Its imaging speed can be much faster than the conventional imaging system using a single detector with mechanically scanned optics. We are using a Yagi-Uda antenna with Schottky diodes on a dielectric substrate lens. This year we calculated the impedance of the Yagi-Uda antenna to obtain optimum impedance for the Schottky diode. We have successfully obtained an antenna pattern suitable for the imaging optic and an antenna impedance good for the Schottky diode by tuning the director element of the Yagi-Uda antenna. Furthermore, a patch antenna array has been studied, which has advantages for incorporating MM wave integrated circuits on a dielectric substrate with the antennas and the diode chips.

When active elements such as Gunn diodes or field effect transistors (FETs) are used in the quasi-optical multi-element array, the array becomes a coherent power combiner which is useful in the MM wave and higher frequency regions. The quasi-optical oscillator consists of a grooved mirror mounted with Gunn diodes and an opposing concave spherical mirror. We have successfully obtained coherent power combining with three Gunn diodes at 50 GHz, which is shown by improvement of the signal-to-noise ratio of the output signal in comparison to that of the output from a single diode oscillator.

Frequency multipliers using Schottky diodes are also useful as a tunable source in the THz region. We have obtained the 12th harmonic (1.2 THz) of the incident 100 GHz millimeter wave power. We measured transmission characteristics of wave guide cut-off filters with cut-off frequencies of 260 GHz and 400 GHz by using the third and the fourth harmonics as the signal. The measured cut-off characteristics have good agreements with theoretically calculated values.

Research of High-Frequency Optical Waveguide Modulators

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In this work, matching between the optical wave and modulating wave phase velocity, a new structure of traveling wave optical modulator, is proposed. Characteristics and design of the modulator have been analyzed and calculated exactly.

In order to manufacture the devices it is necessary to develop three-dimensional fine process technology which fabricates a few micron steps with vertical and smooth sidewalls using dielectrics and semiconductors for optical waveguides, and metals for electrodes.

We report a summary of this study and experimental results such as etching of dielectrics, semiconductors, and metals by using dry etching apparatus and etching gases.

Aono Atomcraft Project

Masakazu Aono
Project Director

1. Introduction

Today, various artificial superlattices are being created by controlling the deposition of material at the level of atomic layers. In the not too distant future, however, an even finer control of the material structure will be required in order to achieve even greater control of the material function. Thus, the material structure must be controlled not only at the level of atomic layers, but at the level of atoms themselves.

The "Atomcraft" Project is searching for new methods for controlling the structure of solid surfaces at the level of atoms. The new methods represent a departure from the current evolution of semiconductor microfabrication technology, since they involve rather advanced applications of current surface science. This is the reason why the newly coined word "atomcraft" is being used as the title of this project.

The Atomcraft Project, which started one year ago, consists of the following three groups: Basic Analysis, Structure Control, and Surface Measurement Groups. The three groups focus their research on developing novel methods for depositing material in an atom-by-atom manner and supplying energy into small "atomscopic" regions on solid surfaces in strong mutual cooperation. The present status of the three groups is as follows.

2. Basic Analysis Group

The main aim of this group is to predict the behavior of atoms on solid surfaces in various conditions through theoretical simulations using a supercomputer. The resulting knowledge will hopefully clarify which types of structural control are possible and which are not. Computer codes necessary for this purpose have already been developed and first applied to analyze the behavior of silver atoms on a silicon surface. Analysis of the interaction of slow ions with surface atoms has also been started. An experimental subgroup is constructing a scanning tunneling microscope of a new type in which the transfer of atoms between a tip and a sample surface can be directly observed.

3. Structure Control Group

The main purpose of this group is to develop novel methods for depositing material in an atom-by-atom manner and to supply energy into atomscopic regions on solid surfaces. This is achieved with the aid of theoretical simulations done in the Basic Analysis Group and new methods for analyzing the resulting surfaces developed in the Surface Measurement Group. So far, three

methods for the deposition of material and two methods for the supply of energy have been designed and instruments for these purposes are now being constructed.

An apparatus for layer-by-layer composition-controlled molecular beam epitaxy growth with the aid of monitoring by coaxial impact-collision ion scattering spectroscopy has also been constructed.

4. Surface Measurement Group

In the Atomcraft Project, scanning tunneling microscopy is often used, but this technique cannot identify the species of individual atoms in observed images of atomic arrangement. One of the most important research subjects of this group is to develop a novel method that solves this inconvenience. A method utilizing certain interaction of slow ions with surface atoms is going to be examined.

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